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ABSTRACT

The discovery of molecules with tailored optoelectronic properties, such as specific frequency and intensity of absorption or emission, is a major challenge in creating next-generation organic light-emitting diodes (OLEDs) and photovoltaics. This raises the following question: How can we predict a potential chemical structure from these properties? Approaches that attempt to tackle this inverse design problem include virtual screening, active machine learning, and genetic algorithms. However, these approaches rely on a molecular database or many electronic structure calculations, and significant computational savings could be achieved if there was prior knowledge of (i) whether the optoelectronic properties of a parent molecule could easily be improved and (ii) what morphing operations on a parent molecule could improve these properties. In this Perspective, we address both of these challenges from first principles. We first adapt the Thomas–Reiche–Kuhn sum rule to organic chromophores and show how this indicates how easily the absorption and emission of a molecule can be improved. We then show how by combining electronic structure theory and intensity borrowing perturbation theory we can predict whether or not the proposed morphing operations will achieve the desired spectral alteration, and thereby derive widely applicable design rules. We go on to provide proof-of-concept illustrations of this approach to optimizing the visible absorption of acenes and the emission of radical OLEDs. We believe that this approach can be integrated into genetic algorithms by biasing morphing operations in favor of those that are likely to be successful, leading to faster molecular discovery and greener chemistry.

I. INTRODUCTION

A. Designer molecules

Conventional electronic structure theory[1,2] has become highly successful at taking a molecular structure as an input and producing molecular properties as outputs [Fig. 1(a)]. However, to our knowledge, there is no widely applicable general theory or algorithm for the reverse process, namely, starting with a list of desired molecular properties and producing a molecule that satisfies them as an output—the inverse design problem [Fig. 1(b)]. This is a shame, since there is huge demand for molecules meeting a given set of criteria, especially in fields such as optoelectronics where there are many (often competing) requirements for the chromophore. These requirements can include a specific absorption/emission wavelength, high oscillator strength, slow internal conversion to the ground state, fast internal conversion to a triplet–triplet state (for singlet fission[3–7]), large singlet–triplet energy gap (for singlet fission), small singlet–triplet gap (for thermally activated delayed fluorescence, TADF[8–10]), and so on. For light-emitting diodes (LEDs), further development of molecular materials will enable realization of efficient and stable blue LEDs that meet the performance of established red and green pixels for displays,[11,12] as well as in infrared devices for optical communications and bio-imaging.[13] Strong light absorption of molecules in the visible range is useful for indoor photovoltaics, where device efficiency can be optimized for lighting conditions by chemical design.[14] This emerging technology presents

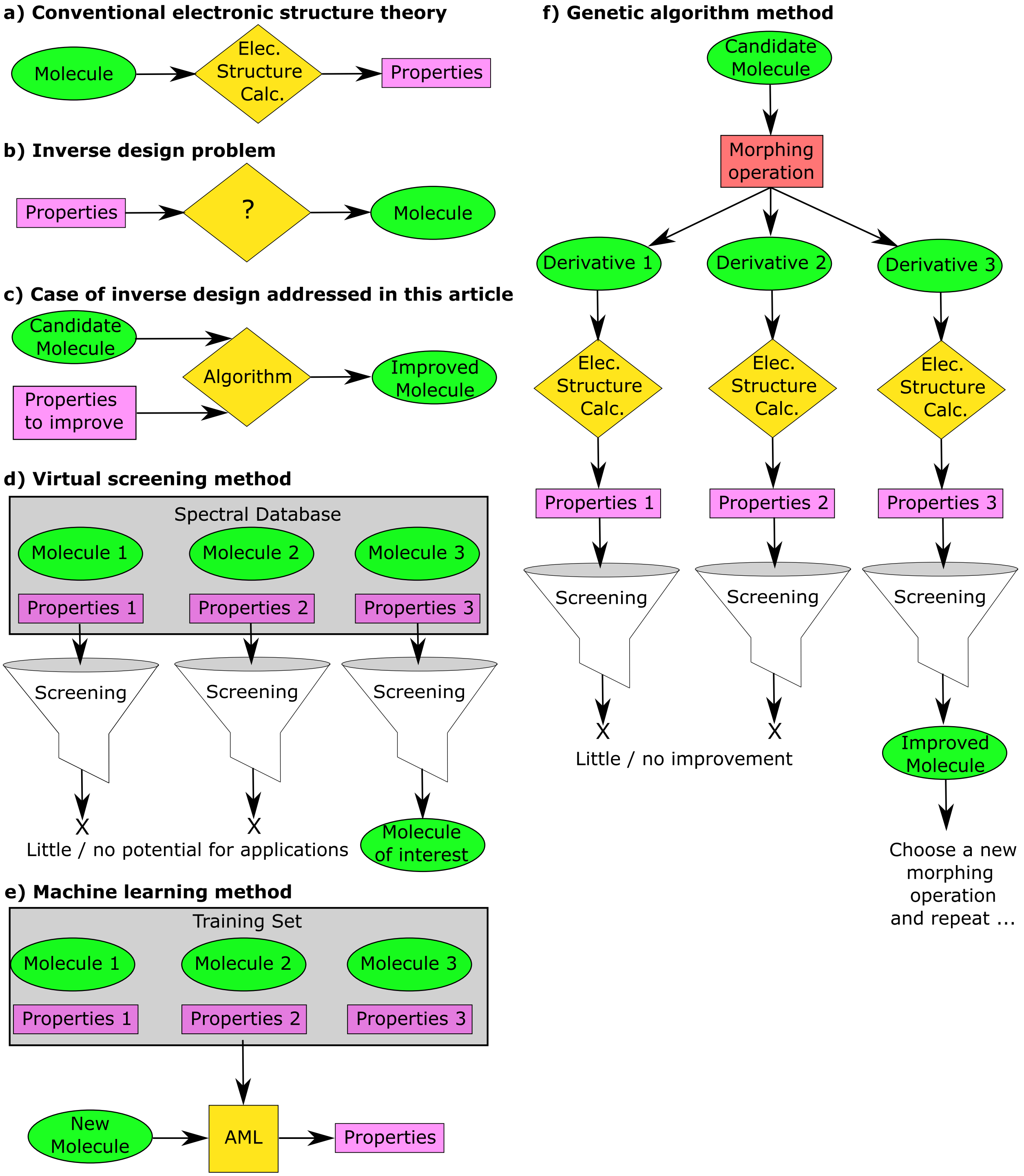

FIG. 1. Flow diagrams illustrating the motivation of this article. (a) Standard electronic structure theory: computing properties from a known molecular structure. (b) The overall challenge: computing a molecular structure from a given set of properties. (c) The case of (b) considered in this Perspective: taking a candidate (parent) molecule and properties to optimize and finding an improved molecule. (d) A virtual screening approach using a known database, but which is constrained by the number of known and documented molecules. (e) A machine learning approach: training an algorithm to rapidly compute the properties of unseen molecules from known chemical data. (f) A genetic algorithm approach: morphing operations to a first generation molecule, computing the properties of the mutated molecules, and screening and repeating for multiple generations.

opportunities for the design of new molecules tailored for these applications and, hence, motivates a general theory for solving the inverse design problem.

This Perspective considers a more specific version of the inverse design problem in Fig. 1(b), namely, starting with (i) a parent molecule that has reasonable, but not ideal, properties and (ii) knowledge of which of these properties require modification, and from these inputs producing (iii) an improved molecule that better satisfies the desired properties in (ii), as shown schematically in Fig. 1(c). In this Perspective, we show how by combining electronic structure theory and quantum mechanical perturbation theory, we can provide a general theoretical and computational framework from first principles for achieving this *without extensive computation or chemical synthesis*. Furthermore, by applying pre-existing theory to the inverse design problem, we obtain three major principles of chromophore design, summarized as follows:

Three Major Principles of Chromophore Design

1. When considering different isomers of a chromophore, oscillator strength can neither be created nor destroyed but only moved from one region of the spectrum to another.
2. For substitution, excitations mix if and only if they differ by (at maximum) one orbital and the orbitals by which they differ both have amplitude on the substituted atom.
3. For addition and dimerization, using a zeroth-order Hamiltonian of separated monomers:
   (a) Leads to zeroth-order states that have exclusively Local Excitation (LE) or Charge Transfer (CT) character, are strictly orthogonal, and form a complete singly excited basis;
   (b) Leads to CT states that at zeroth-order are always dark and whose energies are given by Koopman's theorem, but at first order (and above) can borrow intensity from bright LE states, and whose first-order energy correction is dominated by Coulombic stabilization;
   (c) LE states mix with CT states through one-electron terms (transfer integrals), which can be determined from examining monomer molecular orbitals and from the relative geometry of monomer units in the dimer;
   (d) LE states mix with other LE states, and CT states with other CT states, via electrostatic terms, which can be estimated from the monomers' multipoles and their relative geometry. The LE/LE mixing can be approximated by the Kasha dipole–dipole interaction.

In this Perspective, we derive these rules and provide examples of their applicability.

This Perspective is far from the first article to address the inverse design of chromophores,[15–17] and current methods fall into three broad groups. The first is the virtual screening (VS) approach [Fig. 1(d)] that comprises screening known molecules in a database against design criteria using molecules' properties contained within the database or computed on the fly, as shown in Fig. 1(d).[18] This approach is limited by the size of the database and the quality and quantity of data therein, and any database stored on a modern computer is likely to include only a tiny fraction of chemical space. VS alone is limited in its scope as a prediction tool as it does not offer any new information about potential new molecules, even those that are similar to, or derivatives of, those in the database.

The second approach is active machine learning (AML) [Fig. 1(e)] where trends in chemical or physical properties are inferred by comparing the properties of a large set of molecules, called a training set, using statistical algorithms, such as regression [e.g., Gaussian Processes Regression (GPR)], deep learning (DL), and artificial neural networks (ANN) among others.[19] The training set is taken from a database[20] or generated by successively applying morphing operations to a parent molecule.[15,21] AML offers more predictive power than VS in the sense that it can 'learn' from the data being given to it in order to make predictions about unseen data.[22] However, its predictive power is limited by the size and variation of data in the user-defined training set, as predictions about data outside the space of the training set (i.e., extrapolation) can be unreliable. Despite these limitations, AML algorithms have had much success in rapidly predicting chemical and physical properties of atoms and molecules, saving computational effort.[20,23,24]

Finally, there is the genetic algorithm (GA) approach[25,26] [Fig. 1(f)] in which a parent molecule is altered using morphing operations, producing "second generation" molecules that have chemical properties computed for them. These second generation molecules are then screened against a design criterion and those that pass the screening process are then kept and the remainder discarded. The process is then repeated for many generations with many possible morphing operations until a suitable molecule is found. The screening is based on a fitness function, calculated from one or more properties of the molecule, which aims to quantitatively describe how well suited a molecule is for the applications. Those molecules that pass the screening process must exceed a threshold value of the fitness function. The success of the GA approach is crucially dependent on (i) whether the properties of the parent molecule can be improved and (ii) whether the chosen morphing operations can improve these properties. Hence, there have been efforts in combining GA and AML for the molecular design (see Fig. 1 of the supplementary material), where AML is used to predict which are the most productive morphing operations to be applied to each successive generation.[15,21,27,28]

B. Molecular design challenges

Machine learning, genetic algorithms, and combinations of the two are perhaps the best current approaches in the field of molecular design but still have various challenges, namely:

1. It is not usually known at the outset whether or not, and to what extent, the properties of the first generation molecule can be improved before many calculations are run.
2. It is not usually known whether the proposed morphing operations will, or can, lead to any improvement, and if they can, where on the molecule they should be made, or how many are required, without running many electronic structure calculations.

Taken together, these challenges mean that, until a full AML/GA calculation is run, it is difficult to know whether, and to what extent, it will be successful. Due to the large size of chemical space and the need for accurate property computation, the calculations can therefore be extremely expensive. It would therefore be very helpful to have an indication, in advance of a full calculation, of whether any improvement is possible and if so what morphing operations should be made. In this Perspective, we address both the challenges given above for the case of electronic absorption and emission intensity (and energy) in specific regions of the spectrum, an area of huge interest for optoelectronic applications.

We stress that the above challenges are not reasons to avoid machine learning and genetic algorithms—quite the converse. We hope that the theoretical toolkit proposed in this Perspective can be used to inform these algorithms and accelerate the discovery of new useful molecules for optoelectronic applications.

To address the first challenge, we show how the Thomas–Reiche–Kuhn sum rule can be used to provide much lower bounds on the total oscillator strengths of molecules than are usually quoted,[2,29] giving a more realistic maximum of the total low-energy absorption that can be expected. To address the second challenge, we combine electronic structure theory[1] with intensity borrowing perturbation theory[30] to construct a theoretical framework for describing how morphing operations to a parent molecule are likely to change the electronic structure of its offspring. Crucially, this requires only the knowledge of the electronic structure of the parent molecule and very basic knowledge of the alteration (for substitution, which atoms will be changed, and for addition and dimerization, the relative geometry of monomers). This does *not* require a separate full electronic structure calculation for each possible morphing operation. Using this theoretical framework, we show how it is possible to predict whether and which morphing operations are likely to increase the absorption or emission in a particular region of the spectrum (usually the visible), addressing the second challenge. It is also possible to determine where on the molecule the alterations should be made and to give an approximate idea of the extent to which any given alteration will improve the molecule's properties. Combining these results can then lead to general rules for increasing chromophore absorption and emission. The general methodology is illustrated in Fig. 2.

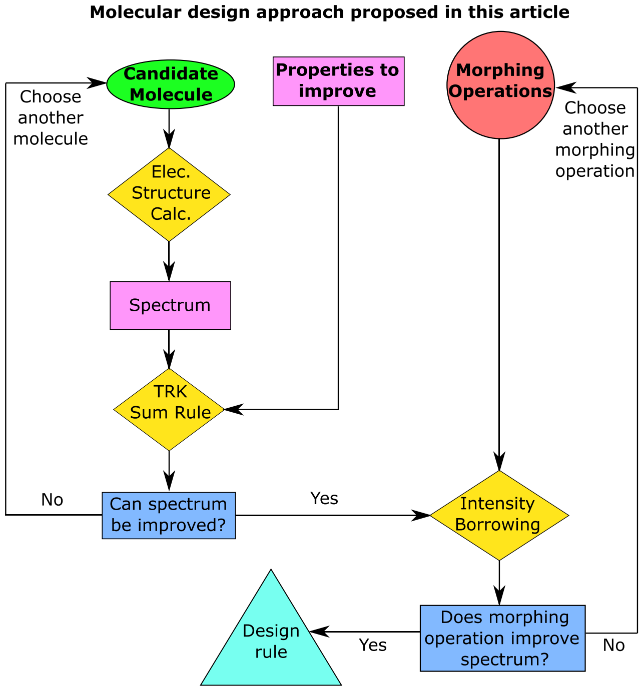

FIG. 2. Flowchart illustrating the general methodology proposed in this Perspective. Starting with a candidate (parent) molecule, properties to be improved, and possible morphing operations, we show how by combining intensity borrowing perturbation theory and electronic structure theory, we can predict which morphing operations are likely to be successful and thereby formulate design rules.

C. What to optimize?

For light-emitting optoelectronics, such as organic light-emitting diodes (OLEDs), emission is usually from the lowest bright excited state, usually S_1 for ground-state closed shell molecules and D_1 for radicals. The rate of emission is given by the Einstein transition coefficients,[2] which, in turn, depend on the transition dipole moment of the $S_1 \rightarrow S_0$ transition (or $D_1 \rightarrow D_0$ for monoradicals). A key requirement for high-efficiency OLEDs is for the rate of radiative decay, k_r, to exceed the rate of non-radiative decay, k_{nr}, such as reaching the ground state via an avoided crossing or conical intersection. Consequently, a goal for OLED design is to maximize the dipole moment associated with the $S_1 \rightarrow S_0$ transition. An added complication for ground-state closed-shell species is the dark triplet state T_1, which is usually a loss pathway, though can be brightened by phosphorescence or can emit indirectly through reverse intersystem crossing (RISC) in thermally activated delayed fluorescence (TADF) devices.[8,9]

Conversely, for light-absorbing optoelectronics, such as photovoltaic cells, the priority is usually absorbing as much light as possible within the solar spectrum, which is principally concentrated in the visible (roughly 400–700 nm in wavelength). This can be achieved by having a lowest-lying excited state with very broad absorption or by having multiple absorptions in the visible. In the latter case, a molecule absorbing above the S_1 state usually undergoes rapid internal conversion to S_1 such that most photophysics of interest, such as charge generation, occurs from the S_1 state. Exceptions to this include intramolecular singlet fission,[3–5,31–34] where the lowest bright state undergoes internal conversion to a (usually dark) triplet–triplet state. Many common organic molecules, such as acenes, have intense absorption in the UV (where there is less solar irradiance) but weak absorption in the visible, making them ideal candidate molecules for the spectral optimization discussed in this Perspective.

Consequently, for OLEDs, it is of particular interest to increase the transition dipole moment between the ground state and the lowest bright excited state and for photovoltaics to increase absorption in the visible. These are, therefore, the main motivations of the theoretical framework in this Perspective. Although we apply our methodology to the low-lying excited states of conjugated organic molecules (for which there is large interest for optoelectronics), the general theoretical principles can be applied to optimizing any property of a molecule which can be related to a quantum mechanical operator, such as spin–orbit coupling, permanent dipole, and non-adiabatic coupling.

D. The general idea

Clearly, there is an enormous range of chromophore alterations, and in this Perspective, we consider heteroatom substitution, addition, and dimerization, where dimerization can be considered a form of addition where the adduct is identical to the parent chromophore.

The general idea, as illustrated in Fig. 2, is to start with a molecule that has reasonable, but not ideal properties (such as pentacene for visible absorption), properties to improve (visible absorption) and morphing operations (substitution, addition, and dimerization). The electronic Hamiltonian of the parent molecule can be solved at an approximate level of theory, leading to the spectrum of the parent chromophore. In the language of perturbation theory, this defines our zeroth-order Hamiltonian and zeroth-order states. From this spectrum and the TRK sum rule, we can deduce whether or not a molecule has significant potential for improvement (for pentacene, having large absorption in the UV, which could be moved to the visible). For substitution, we then define the morphing operations as perturbations to the zeroth order states (for addition and dimerization, the algebra is similar but more involved) and use intensity borrowing perturbation theory[30] to determine how morphing alterations will alter the spectrum. In the event that the morphing operation does not improve the spectrum, a different one can be tried, and if the spectrum is improved, a design rule can usually be derived.

By construction, a perturbative approach will not give an exact solution for the chromophore's electronic structure (even within an approximate Hamiltonian), but the qualitative results can then be used to guide which morphing operations are more likely to improve the desired property. Much research on organic chromophores has focused on low-energy HOMO → LUMO transitions in organic molecules (whether local excitation or charge-transfer in nature),[3,4,35] and the theoretical results in this Perspective are applicable to single excitations between any occupied and unoccupied orbitals. This can therefore include excitations in the visible, which are higher-lying than the HOMO → LUMO transition, and whose optimization is unlikely to substantially affect the pre-existing photophysics (such as ability to undergo singlet fission) since Kasha's rule[36] implies rapid internal conversion to the lowest excited singlet state.

In this Perspective, we restrict our attention to electronic intensity borrowing, with application to the (generally weaker) effects of vibronic (Herzberg–Teller) coupling[2,37,38] and spin–orbit interactions[2,39,40] left for future research. Although not the main focus of this Perspective, a by-product of intensity borrowing perturbation theory is expressions for perturbed energies, and these can be used to guide how a given alteration can lead to spectral blue shifting or red shifting. In addition, the spectra of organic molecules commonly contain vibrational stretching progressions, which are of experimental and theoretical interest.[41,42] These progressions spread the oscillator strength associated with a single transition over a number of vibronic peaks, but since the sum over Franck–Condon factors is equal to unity,[2] do not increase the total absorption associated with a single electronic transition, and are consequently not the focus of this Perspective. We seek to provide general rules for suggesting which molecules are likely to have improved absorption/emission, rather than high-level calculation on a single molecule for which many methods already exist. Similarly, we do not consider zero-point-energy adjustments,[43] which may be required to accurately replicate experimental spectra.

For construction of a suitable Hamiltonian, there are a wide range of electronic structure methods available of varying computational cost and accuracy, and here we consider the simplest model that describes the necessary physics of organic chromophores. While Hückel theory is arguably the simplest model for simulating arbitrary π systems, it neglects two electron terms so (for example) does not account for the exchange energy of forming a singlet excitation or its Coulomb stabilization, leading to an inaccurate description of excited states.[44] We, therefore, use Pariser–Parr–Pople (PPP) theory,[44–48] which is similar to Hückel theory but also includes two-electron terms within the neglect of differential overlap (NDO) approximation. Early applications of PPP theory include simulating the spectra of acenes[45] and their substituted derivatives,[49–51] and it continues to be widely used[52–63] for the simulation of large conjugated systems. In this Perspective, we use configuration interaction singles (CIS) to describe excited states, since the ground state of many organic chromophores can be reasonably well described by a single restricted-Hartree–Fock (RHF) determinant as the dipole moment is a one-electron operator, meaning that most double and higher excitations are dark.[64] There are, of course, situations where double and higher excitations play an important role, for example, in modeling the triplet–triplet state in singlet fission or the dark doubly excited $2A_g^-$ state in β-carotene. However, in this Perspective, we concern ourselves with describing linear absorption spectra in which single excitations dominate.[1,6] Nevertheless, PPP can be extended to double and higher excitations,[65–67] as could intensity borrowing theory. As we shall see, PPP can accurately describe the spectral phenomena we consider in this Perspective, though for weak interactions (such as Dexter) that rely on orbital overlap, different methods may be required.

There are, of course, many other electronic structure methods that could be used, such as density functional theory (DFT) based approaches. Time-dependent DFT (TD-DFT) can sometimes predict inaccurate energies for CT states due to the incorrect long-range behavior of local exchange-correlation functionals, such as B3LYP, and therefore, one has to employ a modified functional that is corrected for long-range behavior.[68–72] This difficulty in predicting the energies of CT states is particularly problematic for acenes.[73] Alternatively, complete active space methods, such as CASSCF, could in theory be used, but their high computational expense, the difficulty in selecting an active space,[6] and the need to incorporate perturbation theory in order to obtain accurate energies[74] make them unsuited to simulating large numbers of excited states in many candidate molecules.

Although the underlying theories in this Perspective [TRK sum rule, intensity borrowing perturbation theory (IBPT), configuration interaction singles, and PPP theory] have been around for decades, we believe this is the first time the TRK sum rule has been applied to the inverse molecular design problem, for which it could be used to formulate a fitness function. Combining PPP theory and IBPT to predict molecular spectra was, to our knowledge, first proposed in 2019[74] for the specific case of acene dimer absorption, after which it has been applied to the design of radical OLEDs.[75] However, to the best of our knowledge, this is the first time this algebraic framework has been published generally and in full (i.e., not for a single specific application) and the first time it has been presented in the context of the inverse design problem or artificial intelligence approaches.

E. Background chromophore theories

There is clearly a large range of pre-existing chromophore theories that we briefly review here. Since the proposition of the chromophore theory of color in 1876,[76] there have been continued efforts to describe the effects of molecular structure upon optical absorption. Early developments, mainly concerned with excitations in crystals, include the eponymous research on excitons by Frenkel,[77] Wannier,[78] Mott,[79] and Davydov.[80] For molecular absorption, Kasha's exciton model[81] describes chromophore interaction by a point-dipole approximation, and more theoretical approaches include the Thomas–Reiche–Kuhn (TRK) sum rule[2,82–84] and intensity borrowing perturbation theory,[30,85] which are used in this Perspective. Textbook[2] approaches to chromophore properties include the particle-in-a-box model (predicting an intense HOMO → LUMO transition that redshifts with increasing molecular size) and satisfying spin and point group symmetry.

Since then, there has been substantial interest in chromophore alteration and interaction in biological systems, such as porphyrins,[86,87] DNA,[88] and green fluorescent protein;[89,90] in photovoltaic applications,[35,91,92] such as singlet fission;[4,93–95] and in organic light-emitting diodes,[96,97] such as thermally activated delayed fluorescence,[8,9] radical emitters,[75,98,99] and carbene-metal-amides.[100,101] Examination of intermolecular interaction in crystals has led to explanation of crystallochromy,[102] and investigation of single molecule junctions has led to the effects of conformation on intramolecular interaction.[103,104] In addition, tuning the absorption frequency (color) of a chromophore has been achieved by altering the HOMO–LUMO gap with various substituents[35,105–107] and design principles formulated by examining large groups of previously-synthesized or computed chromophores.[35,92]

Despite this progress challenges remain. The absorption of organic molecules in the visible is often a small fraction of the maximum allowed by the TRK sum rule,[29] and it can be unclear how to optimize the chromophore structure to increase absorption intensity (extinction coefficient).[108,109] Rational design principles would arguably have wider and clearer applicability than those obtained empirically,[92] and the large size of chemical space can render a trial-and-error approach inefficient. Nevertheless, the design of highly absorbent chromophores would be of considerable practical benefit, such as enabling the construction of thinner solar cells without attenuating the absorption of light,[29] thereby requiring smaller exciton diffusion and leading to greater photovoltaic efficiency.[110] Similarly, designing OLED emitters with greater intensity of emission (transition dipole moment) would lead to faster radiative decay[2] and a greater likelihood of these outcompeting undesirable non-radiative processes, such as internal conversion.[99]

F. Article structure

In Sec. II, we address the challenge of determining the extent to which a given molecule's spectrum can easily be improved. To do this, we examine the Thomas–Reiche–Kuhn sum rule in Sec. II A and see how this leads to lower limits on UV–vis transitions than is sometimes quoted. We illustrate this by application to a variety of organic chromophores in Sec. II B. We then address the second challenge of predicting where and how a molecule should be substituted, added to, or dimerized in Sec. III. To do this, we first recap pre-existing intensity borrowing theory (Sec. III A). We then apply this theory, using the framework of configuration interaction singles and Pariser-Parr-Pople theory (see Secs. III A 1 and III A 3 of the supplementary material), to substitution in Sec. III B, addition in Sec. III C, and dimerization in Sec. III D. Having addressed these challenges from a theoretical perspective, we then apply the methodology to real chromophores in Sec. IV. We consider improving the visible absorption of acenes in Sec. IV A followed by improving the emission of organic radicals in Sec. IV B. We conclude in Sec. V.

II. CHALLENGE 1: HOW IMPROVABLE IS A MOLECULE?

A. Thomas–Reiche–Kuhn sum rule

Here, we consider the Thomas–Reiche–Kuhn sum rule[82–84] (TRK) theoretically to determine approximate upper bounds to the absorbance of organic chromophores. For a system with N_e electrons, TRK is commonly quoted as[2,29]

$$\sum_{u>0} f_u = N_e, \tag{1}$$

where the oscillator strength f_u of excitation to eigenstate $|\Psi_u\rangle$ is

$$f_u = \frac{2m_e}{3\hbar^2}|\langle\Psi_0|\hat{\mathbf{r}}|\Psi_u\rangle|^2(E_u - E_0), \tag{2}$$

where m_e is the mass of an electron and $\hat{\mathbf{r}}$ is a generalized coordinate vector. As presented in Eq. (1), the TRK refers to excitations from the ground state, though it also holds for any excited state. Qualitatively, Eq. (1) means that the oscillator strength is conserved and that while the oscillator strength can be moved from one area of the spectrum to another [as Eqs. (1) and (2) give no limits on the energy of a transition], it can neither be created nor destroyed, i.e., structural isomers will have the same total oscillator strength for all transitions from the ground state.

Computationally, it is found that low-energy (such as visible) excitations often constitute a tiny fraction of the total allowed oscillator strength,[29] and since only the N_v valence electrons are expected to contribute to low-energy transitions, Eq. (1) is sometimes approximated as N_v.[2] This would suggest that for an organic chromophore with N_π electrons in the π system, the upper limit on oscillator strength would be N_π. However, the derivation of TRK holds in each dimension $\{x, y, z\}$ separately[2] such that

$$\sum_{u>0} f_u^{(x)} = \frac{N_e}{3}, \tag{3}$$

where

$$f_u^{(x)} = \frac{2m_e}{3\hbar^2}\sum_{u>0}|\langle\Psi_0|\hat{x}|\Psi_u\rangle|^2(E_u - E_0) \tag{4}$$

and likewise for y and z. Clearly, Eqs. (3) and (4) are consistent with, but more restrictive than, the TRK in Eq. (1), though in themselves do not suggest a new upper limit for chromophore absorption.

Let us then consider a linear π-system, with atoms aligned along the x axis. Using a basis of p orbitals on each atom (as in Hückel and PPP theory), $\pi \rightarrow \pi^*$ transitions must be x-polarized. This means

TABLE I. Approximate upper bounds on chromophore absorption. N_π is the number of electrons in the π system, and N_v is the number of valence electrons.

Chromophore	$\sum_u f_u$
Linear π system	$N_\pi/3$
Planar π system	$2N_\pi/3$
General	N_v

that the maximum oscillator strength for any linear organic chromophore, which carotenoids (polyenes) can be approximated to be,[29] is $N_\pi/3$, where $f_u^{(x,\pi)}$ refers to x-polarized transitions involving π electrons.

Let us now consider a planar π-system, such as pentacene or tetracene, with atoms in the (x, y)-plane. Using similar arguments to the above, transitions can only be x or y-polarized, meaning that the maximum allowed oscillator strength is $2N_\pi/3$. We see that both the linear and planar limits are smaller upper limits on absorption than N_π for a general three-dimensional chromophore and are summarized in Table I, allowing us to appraise more accurately the extent to which the absorption of a chromophore in the visible (or any other region of the spectrum) is close to the maximum possible or whether there may be scope to increase absorption further.

These results allow us to define an "absorption efficiency" in a spectral region by comparing the integrated oscillator strength[29] in that region with the approximate absorption upper bound to total absorption in Table I. For example, a planar chromophore absorbing in the visible would give

$$\eta_{\text{abs}} = \frac{\sum_{\lambda=400\text{ nm}}^{700\text{ nm}} f(\lambda)}{\frac{2}{3}N_\pi} \tag{5}$$

$$= \frac{2m_e c\epsilon_0}{N_A N_\pi e^2}\int_{4.3\times10^{14}\text{s}^{-1}}^{7.5\times10^{14}\text{s}^{-1}} d\nu\epsilon(\nu), \tag{6}$$

where the frequency is given in Hz. This can be calculated from both theory and experiment, and unlike molar extinction coefficient goes not grow simply by oligomerizing the chromophore.[108] Equation (6) gives a rough guide to whether much of the possible absorption is in the desired region of the spectrum, and there is little scope for improving efficiency, or whether only a small fraction of absorption is in the visible, with substantial scope for improvement by "borrowing intensity" from high-energy transitions. In the context of machine learning, the absorption efficiency in Eq. (6) could be incorporated into a fitness function for optimizing organic chromophores.

B. Typical chromophores

For example, it has been known since the 1930s that much of the oscillator strength of carotenoids is in the $S_0 \to S_1$ transition[85] and higher-energy $\pi \to \pi^*$ transitions are relatively weak. Conversely, acenes have a relatively weak $S_0 \to S_1$ transition and a much more intense transition (x polarized) at higher energies.[45] However, in general, the absorption of hydrocarbons in the visible falls well below the lower limits in Table I. In Fig. 3, we present a selection of common organic chromophores, and in Table II, we compare their absorption with the maxima given by the TRK sum rule. Tetracene, for example, has a transition around 474 nm with an oscillator strength (from early experiments[112]) of 0.08, corresponding to 0.7% of the total possible oscillator strength in the visible region. In the near UV around 275 nm, it has a transition with an

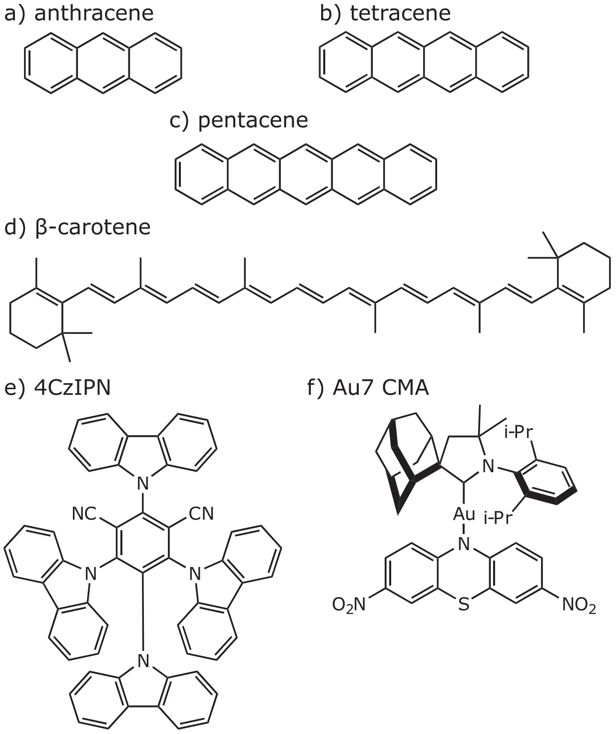

FIG. 3. Structures of example chromophores whose absorption is considered in Table II. β-carotene is an example of a polyene, and acenes anthracene, tetracene, and pentacene are presented. We also include the common TADF molecule 4CzIPN and a carbene-metal-amide (CMA) chromophore, Au7.

TABLE II. Vertical excitation energies and oscillator strengths for a series of π-systems from experimental data and *ab initio* calculations (see Table 1 of the supplementary material for more details).

Chromophore	State	λ	f_{osc}	TRK max.	% of TRK max.
Ethene[111]	$1B_{3u}^+$	163	0.34	0.67 (x)	51
Anthracene[112]	$1B_{2u}^+$	379	0.1	9.33 (x, y)	1.1
	$1B_{3u}^+$	256	2.28		24
Tetracene[112]	$1B_{2u}^+$	474	0.08	12 (x, y)	0.7
	$1B_{3u}^+$	275	1.85		15
Pentacene[112]	$1B_{2u}^+$	585	0.08	14.67 (x, y)	0.5
	$1B_{3u}^-$	417	~0		~ 0
	$1B_{3u}^+$	310	2.2		15
β-carotene[113–115]	$2A_g^-$	~700	0	7.33 (x)	0
	$1B_u^+$	488	2.66		36
4CzIPN (calc.)[116]	B	474	0.05	68 (x, y, z)	0.1
Au7 CMA (calc.)[117]	A_1	434	0.26	36 (x, y, z)	0.7

oscillator strength of 1.85, 15% of the total allowed. Tetracene also has other transitions in the visible that are dark. This suggests that (for tetracene at least) there is substantial scope for improving the visible absorption because (a) the total absorption in the visible is a tiny fraction of the total allowed, (b) there is substantial oscillator strength "nearby" in the spectrum that in theory could be borrowed, and (c) there exist states in the visible that could in theory borrow intensity.

From the results in Table II and in the literature, we can approximately categorize many chromophores:

1. Those whose lowest energy transitions are in the UV (such as ethene), suggesting that increasing their visible absorption is difficult.
2. Those that have intense visible absorption (such as β-carotene) but undesireable photochemical properties, such as a dark S_1 state.
3. Those that have weak absorption in the visible, which could in theory be increased by borrowing intensity from transitions in the UV. Some of these molecules (such as acenes, 4czIPN, and carbene-metal-amides)[100,118] also have favorable optoelectronic properties, such as the ability to undergo singlet fission or TADF.
4. Those whose lowest energy transition is in the near UV that could be redshifted into the visible (such as anthracene),[119] therefore having potential for increased/tailored visible absorption.
5. Those whose lowest energy transition is in the near infrared but which could be blue-shifted into the visible, such as TTM-1Cz (see Sec. IV B 2).

Therefore, we turn our focus away from molecules, such as ethene and β-carotene in categories 1 and 2, for which simple morphing operations are unlikely to significantly improve their optoelectronic properties, and we will leave the cases of red- or blue-shifting the lowest energy electronic transition in categories 4 and 5 for future work. This leaves the molecules in category 3, which are good candidates for improvement, and brings us to the motivation of this Perspective—how can we employ intensity borrowing perturbation theory to improve the weak visible absorption of such molecules?

III. CHALLENGE 2: HOW TO IMPROVE A MOLECULE?

In this section, we consider what morphing operations are likely to work, where to make them upon a molecule, and how many. To do this, we first present the relevant equations from intensity borrowing perturbation theory[30] (IBPT). We then show how this theoretical framework can be applied to substitution, addition, and dimerization of an arbitrary conjugated organic molecule, from which we formulate widely applicable design rules.

A. Some background theory

Although the results presented here are applied to borrowing of linear absorption intensity, the perturbation expressions hold for any well-defined quantum mechanical operator, such as the spin–orbit coupling operator or nonadiabatic derivative coupling. In this Perspective, as in the original IBPT article,[30] we consider perturbing states rather than orbitals.

As in standard perturbation theory,[2] we define our system as

$$\hat{H} = \hat{H}_0 + \hat{V}, \tag{7}$$

where $\hat{H}_0$ is our zeroth-order Hamiltonian and $\hat{V}$ is the perturbation. We begin with a set of zeroth-order eigenstates $\left|\Psi_u^{(0)}\right\rangle$ where $\hat{H}_0\left|\Psi_u^{(0)}\right\rangle = E_u^0\left|\Psi_u^{(0)}\right\rangle$ and $\{u, v, w\}$ are indices for eigenstates, and we assume the eigenstates to be real, as in generally the case for stationary electronic structure calculations. For generality and unlike Ref. 30, we do not split $\hat{H}_0$ into a "molecule" and "perturber" part, nor factor $\left|\Psi_u^{(0)}\right\rangle$ into a product of molecule and perturber contributions.

As in the previous literature,[30] we only consider transitions from the ground electronic state, though excitations between excited states can be treated similarly. From perturbation theory (see Sec. III A 2 of the supplementary material), we find the leading first-order perturbation to the transition dipole moment of the state $\left|\Psi_u^{(0)}\right\rangle$ to be

$$\left\langle\Psi_0\middle|\hat{\mu}\middle|\Psi_u^{(1)}\right\rangle = \sum_{v\neq u}\left\langle\Phi_0\middle|\hat{\mu}\middle|\Psi_v^{(0)}\right\rangle\frac{\left\langle\Psi_v^{(0)}\middle|\hat{V}\middle|\Psi_u^{(0)}\right\rangle}{E_u^0 - E_v^0} \tag{8a}$$

$$= \sum_{v\neq u}\sum_{ij'} S_{v,ij'}^{(0)}\left\langle\Phi_0\middle|\hat{\mu}\middle|\Phi_i^{j'}\right\rangle \times \frac{\sum_{kl'} S_{v,kl'}^{*(0)}\left\langle\Phi_k^{l'}\middle|\hat{V}\sum_{rs'} S_{u,rs'}^{(0)}\middle|\Phi_r^{s'}\right\rangle}{E_u^0 - E_v^0}, \tag{8b}$$

where we use the definition of the CIS expansion of the state,

$$\left|\Psi_u^{(0)}\right\rangle = \sum_{i,j}\left|\Phi_i^{j'}\right\rangle S_{u,ij'}^{(0)}. \tag{9}$$

We must emphasize that throughout this Perspective, we will refer to the singlet spin-adapted configuration $\left|\Phi_i^{j'}\right\rangle$ corresponding to the excitation of an electron from orbitals i to j' as an *excitation* and a *state* $|\Psi_u\rangle$ as a linear combination of *excitations* [Eq. (9)]. The first-order correction to the energy of state $\left|\Psi_u^{(0)}\right\rangle$ is

$$E_u^{(1)} = \left\langle\Psi_u^{(0)}\middle|\hat{V}\middle|\Psi_u^{(0)}\right\rangle. \tag{10}$$

Unless stated otherwise, the molecular design rules in this Perspective are all obtained using Eq. (8b).

B. Where to substitute?

Here, we combine IBPT, CIS, and PPP theory to inform where an organic chromophore should be substituted to achieve a desired spectral alteration. We first define the zeroth order and perturbation Hamiltonians, followed by the zeroth-order eigenstates, and then see how they are mixed by substitution.

For cases of heteroatom substitution, the zeroth-order Hamiltonian is simply that of the base molecule, and to a first approximation, for a set of atoms $\mathcal{G}$ that are substituted, the perturbation is[50]

$$\hat{V} = \sum_{\mu \in \mathcal{G}} \Delta\epsilon_\mu \hat{n}_\mu, \tag{11}$$

where $\hat{n}_\mu$ is the number operator for the number of electrons on atom μ,

$$\hat{n}_\mu = \sum_{\sigma = \{\uparrow,\downarrow\}} \hat{n}_{\mu,\sigma}, \tag{12}$$

$$\hat{n}_{\mu,\sigma} = \hat{a}^\dagger_{\mu,\sigma} a_{\mu,\sigma}, \tag{13}$$

where $\hat{a}^\dagger_{\mu\sigma}$ and $\hat{a}_{\mu\sigma}$ are the creation and annihilation operators, respectively, for a spin orbital of spin σ on atom μ. ϵ_μ is the on-site energy, which for a purely hydrocarbon chromophore we can set to zero without affecting the energies of excited states. In quantitative applications of PPP theory for heteroatoms,[120] heterosubstitution will also change the $t_{\mu\nu}$ (hopping) and $\gamma_{\mu\nu}$ (repulsion) parameters. However, here we focus on the effect of changing the on-site energy (Hückel α parameter), which affects the diagonal elements of the Fock matrix only,[121] as we find this to be sufficient to derive predictive design rules for substitution.

For substitution, the zeroth-order orbitals $|\phi_i\rangle$ are those that diagonalize the zeroth-order Fock matrix obtained from $\hat{H}_0$, corresponding to the orbitals of the unsubstituted chromophore. The zeroth order eigenstates $|\Psi_u\rangle$ and expansion coefficients $S_{u,ij'}$ are obtained by diagonalizing the CIS Hamiltonian for the unsubstituted chromophore (see Sec. III A 1 of the supplementary material).

From Eq. (11), the perturbation is a one-electron operator,[50] so we can define the change in the Fock matrix as

$$F^{(1)}_{ij} = \sum_{\mu \in \mathcal{G}} \Delta\epsilon_\mu C_{\mu i} C_{\mu j}, \tag{14}$$

where, as above, $\mathcal{G}$ is the set of substituted atoms. We find the perturbation to the Hamiltonian to be

$$\left\langle \Phi_i^{j'} \middle| \hat{V} - \Delta E_0 \middle| \Phi_k^{l'} \right\rangle = \delta_{ik} F^{(1)}_{j'l'} - \delta_{j'l'} F^{(1)}_{ik}, \tag{15a}$$

$$\langle \Phi_0 | \hat{V} \left| \Phi_i^{j'} \right\rangle = F^{(1)}_{ij'}, \tag{15b}$$

$$\Delta E_0 = \sum_{i\ \mathrm{occ}} \sum_{\mu \in \mathcal{G}} \Delta\epsilon_{\mu\mu} C^2_{\mu i}. \tag{15c}$$

From this, we immediately see the following:

Principles of chromophore design for substitution

Substitution will only mix excitations:

1. That differ by one orbital from each other.
2. When the orbitals that differ both have amplitude on the atom that is being substituted.

Both these conditions can be determined by inspection of the monomer spectrum and orbitals and do not require separate calculation for each possible derivative.

For states that are described by linear combinations of excitations, a similar analysis shows that they will only mix if there are excitations in each of the states that differ by at most one electron from each other. If the states consist of the same excitations, but with different expansion coefficients, substitution could alter the diagonal energy of each excitation [Eq. (15a)] and, therefore, the weighting of those states in the configuration interaction expansion, leading to alteration in absorption intensity.

We note that the perturbations in Eq. (15) require minimal extra computation than a monomer calculation, and since the effect of substitution is (to first order) additive, contributions from different substitutions can simply be added removing the need to simulate each possible derivative separately.

For the case of mixing two excitations, where are of different symmetry in the parent chromophore, and for the mixing element to be nonzero, the perturbation $\hat{V}$ must lower the symmetry of system such that in the new, lower, point group, $\left|\Phi_i^{j'}\right\rangle$ and $\left|\Phi_k^{l'}\right\rangle$ transform as the same irreps. This is consistent with previous results examining the effects of aza-substitution on the polarization of transitions.[50]

C. Where to add?

As we shall see, the algebra for addition and dimerization is more complex than for substitution, but the general methodology is the same. We define a zeroth-order Hamiltonian, which in this case corresponds to the two monomers at infinite separation, and then a perturbation Hamiltonian of their interaction when bonded together. We find the zeroth-order orbitals and states, showing that they are exclusively Local Exciton (LE) or Charge-Transfer (CT) in character, and then see how addition mixes these. This leads naturally to many pre-existing chromophore theories.

1. Hamiltonian definitions

For simplicity, we consider an overall chromophore formed from adding one monomer m with set of atoms $\mathcal{M}$ to one other monomer n with set of atoms $\mathcal{N}$, though these ideas can be extended to oligomers.[122] We then imagine taking the two chromophores to infinite separation such that they can be described as a sum of separate Hamiltonians,

$$\hat{H}_0 = \hat{H}_m + \hat{H}_n, \tag{16}$$

where

$$\begin{aligned} \hat{H}_m = {} & \sum_{\mu \in \mathcal{M}} \epsilon_\mu \hat{n}_\mu + U_{\mu\mu} \hat{n}_{\mu,\uparrow} \hat{n}_{\mu,\downarrow} \\ & - \sum_{\mu < \nu \in \mathcal{M}} \sum_{\sigma} t_{\mu\nu} \left(\hat{a}^\dagger_{\mu\sigma} \hat{a}_{\nu\sigma} + \hat{a}^\dagger_{\nu\sigma} \hat{a}_{\mu\sigma} \right) \\ & + \sum_{\mu < \nu, \in \mathcal{M}} \gamma_{\mu\nu} (\hat{n}_\mu - Z_\mu)(\hat{n}_\nu - Z_\nu) \end{aligned} \tag{17}$$

and likewise for H_n, where the notation $\sum_{\mu<\nu,\in\mathcal{M}}$ is taken to mean summation over all μ in $\mathcal{M}$ and summation over all $\nu > \mu$, where ν is also in $\mathcal{M}$. $U_{\mu\mu}$ is the on-site (Hubbard) repulsion and $\gamma_{\mu\nu}$ is the parameterized repulsion between an electron on atom μ and an electron on atom ν, approximating the two-electron integral

$$\gamma_{\mu\nu} \simeq (\mu\mu|\nu\nu) = \int d\mathbf{r}_1 \int d\mathbf{r}_2\ \chi_\mu(\mathbf{r}_1) \chi_\mu(\mathbf{r}_1) \frac{1}{r_{12}} \chi_\nu(\mathbf{r}_2) \chi_\nu(\mathbf{r}_2), \tag{18}$$

where $\chi_\mu(\mathbf{r})$ is the atomic spatial orbital on atom μ, and we use the chemists' notation[1] for two-electron integrals. We then consider bringing the two chromophores back together from which to calculate the perturbation

$$\hat{V} =: \hat{H} - \hat{H}_0 \tag{19a}$$

$$= -\sum_{\mu\in\mathcal{M},\nu\in\mathcal{N}}\sum_{\sigma} t_{\mu\nu}(\hat{a}^\dagger_{\mu\sigma}\hat{a}_{\nu\sigma} + \hat{a}^\dagger_{\nu\sigma}\hat{a}_{\mu\sigma}) + \sum_{\mu\in\mathcal{M},\nu\in\mathcal{N}}\gamma_{\mu\nu}(\hat{n}_\mu - Z_\mu)(\hat{n}_\nu - Z_\nu). \tag{19b}$$

The idea of describing multichromophore interaction as a sum of individual chromophore terms and their mutual interaction dates back to Kasha exciton theory,[81] though the form of the perturbation we obtain in Eq. (19) is more complex than a point-dipole interaction and, as we shall see later, able to describe a wider range of phenomena. The Hamiltonian structure used in Eqs. (17) and (19) has been previously obtained by using PPP theory to describe interchromophore interactions,[53,55] though here it is used to construct a zeroth-order Hamiltonian and perturbation, which causes intensity borrowing, rather than used to generate an overall Hamiltonian for the numerical simulation of large systems.

For addition, the Fock matrix associated with H_m, written in the atomic basis where $\mu, \nu \in \mathcal{M}$, is

$$F^{(0)}_{\mu\mu} = \epsilon_\mu + \frac{1}{2}U_{\mu\mu}P_{\mu\mu} + \sum_{\lambda\neq\mu,\lambda\in\mathcal{M}}(P_{\lambda\lambda} - Z_\lambda)\gamma_{\mu\lambda}, \tag{20a}$$

$$F^{(0)}_{\mu\nu} = -t_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{\mu\nu}, \tag{20b}$$

with similar expressions holding for $\mathcal{N}$. If the atoms are on different monomers ($\mu \in \mathcal{M}$ and $\nu \in \mathcal{N}$), then $\gamma_{\mu\nu} = 0$ and $t_{\mu\nu} = 0$ at zeroth order such that $F^{(0)}_{\mu\nu} = 0$, regardless of the orbital coefficients and the density matrix. Consequently, the Fock matrix corresponding to $\hat{H}_0$ is block-diagonal,

$$\mathbf{F}^{(0)} = \begin{pmatrix} \mathbf{F}^{(0)}_m & 0 \\ 0 & \mathbf{F}^{(0)}_n \end{pmatrix} \tag{21}$$

such that $\mathbf{F}^{(0)}_m$ and $\mathbf{F}^{(0)}_n$ can be solved separately for the orbitals on $\mathcal{M}$ and $\mathcal{N}$. This is no surprise, since the electronic structure of two widely separated monomers should simply be that of the isolated chromophores.

We, therefore, define the molecular orbitals $\{\phi_{ni}\}$ and $\{\phi_{mj}\}$, where n and m refer to the monomers upon which the orbitals are located and i, j, k, l are arbitrary orbital indices. From this, we can form our ground-state (unexcited) wavefunction as the Slater determinant,

$$|\Phi_0\rangle = |\phi_{n1}\alpha, \phi_{n1}\beta, \ldots, \phi_{ni}\alpha, \phi_{ni}\beta, \ldots, \phi_{n,K_n/2}\alpha, \phi_{n,K_n/2}\beta, \phi_{m1}\alpha, \phi_{m1}\beta, \ldots, \phi_{mi}\alpha, \phi_{mi}\beta, \ldots, \phi_{mK_m/2}\alpha, \phi_{mK_m/2}\beta\rangle, \tag{22}$$

where K_n is the number of electrons on monomer n and likewise for K_m and α and β denote the spin component of the orbital. Note we assume here that the molecule is a ground-state singlet, but this can be extended to systems such as radicals with non-zero ground-state spin.[75]

2. Zeroth order excitations: Local exciton or charge transfer

We write single excitations as $|\Phi^{qj'}_{pi}\rangle$, corresponding to a singlet spin-adapted[1] excitation from orbital pi to qj, where $p, q \in \{n, m\}$ (see Sec. III A 1 of the supplementary material). There are consequently two forms of excitation:

1. $p = q$, such as $|\Phi^{nj'}_{ni}\rangle$. This corresponds to an intramonomer excitation, commonly called a local or Frenkel excitation.[3,94,122,123] We, therefore, define $|\mathrm{LE}^{nj'}_{ni}\rangle =: |\Phi^{nj'}_{ni}\rangle$.
2. $p \neq q$ such as $|\Phi^{mj'}_{ni}\rangle$, which is an intermonomer excitation, commonly called a charge-transfer (CT) excitation.[3,94,122,123] Note that these are sometimes referred to as charge-resonance excitations,[124–126] which we refrain from using to avoid confusion with the Coulson–Rushbrooke theorem. We, therefore, define $|\mathrm{CT}^{mj'}_{ni}\rangle = |\Phi^{mj'}_{ni}\rangle$.

The idea of local and charge-transfer excitations has been extensively discussed in the literature,[3,94,122,123,127,128] and the definitions used here are consistent with (for example) Ref. 122. They are sometimes referred to as "diabatic" states,[122,123] terminology we refrain from here since, strictly speaking, they do not necessarily diagonalize the nuclear kinetic energy operator.[129] Other literature defines CT excitations more generally[127] as any transition between a "neutral" ground and an "ionic" excited state. Here, we show LE and CT excitations emerge naturally from our choice of zeroth-order Hamiltonian in Eq. (16) and do not need to be specified *a posteriori*. In addition, our definition of CT and LE states leads immediately to the following useful properties:

1. LE and CT excitations are strictly orthogonal as their constituent MOs are orthogonal,
$$\langle\Phi^{qj'}_{pi}|\Phi^{sl'}_{rk}\rangle = \delta_{pr}\delta_{qs}\delta_{ik}\delta_{j'l'}, \tag{23}$$
and therefore (for example),
$$\langle\mathrm{LE}^{mj'}_{mi}|\mathrm{CT}^{nl'}_{mk}\rangle = 0 \tag{24}$$
for all possible $\{i, j, k, l\}$. This property does not necessarily hold if charge transfer excitations are defined in terms of *dimer* molecular orbitals,[124,127] which when rotated to the *monomer* basis may have local exciton character.
2. LE and CT excitations form a complete basis of singly excited states. This result, while useful, should be interpreted with caution since bases of singly excited states constructed from different MOs do not necessarily span the same part of Hilbert space. We also note that upon extension to double and higher excitations, excitations can have both local and charge-transfer character, such as $|\Phi^{nk'ml'}_{ninj}\rangle$.
3. The definition of LE and CT excitations is unique for two given monomers and independent of their relative orientation, since there are no intermonomer interaction terms in

$\hat{H}_0$ [Eq. (17)] or $\mathbf{F}^{(0)}$ [Eqs. (20) and (21)]. This property does not usually hold if LE and CT states are determined from a RHF (or DFT) calculation on the dimer or oligomer, and it simplifies comparison between different isomeric dimers since they will have the same zeroth-order bases. More practically, the independence of the basis to intermonomer geometry can be useful when the relative orientation of monomeric units is variable or unknown, such as in amorphous films.

4. The zeroth-order basis functions and their zeroth-order energies (including the CT excitations) can be determined from calculations on the respective, independent, monomer units and does not require a separate calculation for each orientation or isomer of the dimer.
5. The transition dipole moment for an LE excitation is

$$\langle\Phi_0|\hat{\mu}\Big|\mathrm{LE}_{ni}^{nj'}\Big\rangle = \sqrt{2}\langle\phi_{ni}|\hat{\mu}|\phi_{nj'}\rangle, \tag{25}$$

which is the dipole moment of the monomer transition, as to be expected, where the factor of $\sqrt{2}$ arises from spin-adaptation of the singly excited wavefunction.[1] This means that for a LE to be bright, the excitation must be allowed in the point group of the monomer, which is generally a more restrictive requirement than for a lower-symmetry dimer.

6. CT excitations are always dark at zeroth order,

$$\langle\Phi_0|\hat{\mu}\Big|\mathrm{CT}_{ni}^{mj'}\Big\rangle = \sqrt{2}\langle\phi_{ni}|\hat{\mu}|\phi_{mj'}\rangle \tag{26a}$$

$$= -\sqrt{2}\sum_{\mu\in\mathcal{M}} C_{\mu,ni}C_{\mu,mj}\mathbf{r}_\mu - \sqrt{2}\sum_{\mu\in\mathcal{N}} C_{\mu,ni}C_{\mu,mj}\mathbf{r}_\mu \tag{26b}$$

$$= 0. \tag{26c}$$

In the first line, we have used the standard result for a one-electron operator,[1] and in the second line, we have used the PPP expression for the dipole moment,[45] choosing to sum over each monomer separately, and the minus sign arises from the negative charge of the electron.[1] However, for the first term in Eq. (26b), $C_{\mu,ni} = 0$ for $\mu \in \mathcal{M}$ (since a monomer orbital entirely on n has no amplitude on any atom on m), and in the second term, $C_{\mu,mj} = 0$ for $\mu \in \mathcal{N}$ (since a monomer orbital entirely on m has no amplitude on any atom on n). This result leads to significant simplifications in the following algebra, since the absence of oscillator strength at zeroth order means that CT excitations must borrow intensity from a LE in order to appear bright and that intensity cannot be "borrowed" from CT states. This result does not usually hold if LE and CT excitations are determined from dimer MOs where the dimer orbitals may not be spatially separated, and the CT excitations computed in the dimer orbitals (which may be bright) correspond to states that are mixtures of CT and LE excitations in the monomer orbitals. This definition also means that if the zeroth-order orbitals are used to compute the dimer excited states at zeroth order, they are exclusively LE or CT, and when computed at first order, it is straightforward to unambiguously compute the extent of LE or CT character. It is clear that the zeroth-order states alone are generally not sufficient to describe the excited states of the dimer; for example, it is known that CT states (strictly speaking, states with CT character) are generally not dark,[127,128,130–133] and we will go on to show how perturbation theory accounts for this.

These results are true for monomers at infinite separation with and without NDO and true for monomers brought together within PPP theory. For a general calculation (at finite separation and without NDO), Eqs. (26), (23), and (24) are expected to hold approximately, though may be non-zero due to the basis functions of one monomer being non-zero in the same region of space as the basis functions of the other monomer.

3. Zeroth order eigenstates: Exclusively LE or CT

The results in Sec. III C 2 are derived for the *basis* of LE and CT excitations, and we now determine the zeroth-order *eigenstates*, obtained by diagonalizing the CIS Hamiltonian.

To simplify the zeroth-order CIS matrix, we first note that at zeroth order, $\gamma_{\mu\nu} = 0$ unless μ and ν are on the same monomer such that two electron integrals are zero unless of the form $(ninj|nknl)$ or $(mimj|mkml)$ for all $\{i, j, k, l\}$. Similarly, the density matrix elements $P_{\mu\nu}$ are zero if μ and ν are on different monomers, since for any monomer orbital pi, either $C_{\mu pi}$ or $C_{\nu pi}$ will be zero.

Since the zeroth order orbitals (by construction) diagonalize the zeroth-order Fock matrix, the zeroth-order Hamiltonian matrix elements are

$$\Big\langle\mathrm{LE}_{ni}^{nj'}\Big|\hat{H}_0 - E_0\Big|\mathrm{LE}_{nk}^{nl'}\Big\rangle = \delta_{ik}\delta_{j'l'}(F_{nj'nj'} - F_{nini}) + 2(nj'ni|nknl') - (nj'nl'|nkni), \tag{27a}$$

$$\Big\langle\mathrm{LE}_{ni}^{nj'}\Big|\hat{H}_0\Big|\mathrm{CT}_{nk}^{ml'}\Big\rangle = 0, \tag{27b}$$

$$\Big\langle\mathrm{LE}_{ni}^{nj'}\Big|\hat{H}_0\Big|\mathrm{CT}_{mk}^{nl'}\Big\rangle = 0, \tag{27c}$$

$$\Big\langle\mathrm{LE}_{ni}^{nj'}\Big|\hat{H}_0\Big|\mathrm{LE}_{mk}^{ml'}\Big\rangle = 0, \tag{27d}$$

$$\Big\langle\mathrm{CT}_{ni}^{mj'}\Big|\hat{H}_0 - E_0\Big|\mathrm{CT}_{nk}^{ml'}\Big\rangle = \delta_{ik}\delta_{j'l'}(F_{mj'mj'} - F_{nini}), \tag{27e}$$

$$\Big\langle\mathrm{CT}_{ni}^{mj'}\Big|\hat{H}_0\Big|\mathrm{CT}_{mk}^{nl'}\Big\rangle = 0, \tag{27f}$$

$$\langle\Phi_0|\hat{H}_0\Big|\mathrm{LE}_{nk}^{nl'}\Big\rangle = 0, \tag{27g}$$

$$\langle\Phi_0|\hat{H}_0\Big|\mathrm{LE}_{nk}^{ml'}\Big\rangle = 0, \tag{27h}$$

and these are general, holding without the approximations of PPP theory for monomers at infinite separation. At finite separation, they hold only within NDO (and therefore PPP) but are likely to be approximately true for a general basis set.

Equation (27a) shows that the interaction between two excitations on the *same* monomer is simply the CIS matrix element if that monomer were considered in isolation, as to be expected for an intramolecular Frenkel excitation. Equations (27b) and (27c) show that there is no mixing between Frenkel and CT excitations, and Eq. (27d) that there is no interaction between Frenkel excitations on different monomers at zeroth order. Equations (27e) and (27f) show that CT excitations interact with no other state except themselves and that their diagonal energy is simply the ionization energy of orbital i $(-F_{ii})$ minus the electron affinity of orbital j' $(-F_{j'j'})$, as would be expected upon forming a separated cation and anion using Koopmans' theorem.[1]

The results in Eq. (27) mean that the zeroth order eigenstates are simply the monomer CIS eigenstates and CT excitations from each monomer orbital to each orbital on the other monomer, with an energy given by the orbital energy difference. Since a CIS calculation on the monomers automatically calculates orbital energies, the complete set of zeroth-order eigenstates and their energies can be obtained at no greater computational cost than calculations on the separate monomers. Since CT and LE *excitations* do not mix with each other at zeroth order, the zeroth-order eigenstates will be purely LE or CT in character such that the results obtained in Sec. III C 2 still apply. Often electronic states of interest are dominated by a single excitation, though the results can easily be extended to states that are linear combinations of excitations using Eq. (9). These results easily extend to oligomers (more than two monomers) using a methodology similar to Ref. 122.

These results are summarized in Table III where we compare the CT and LE states obtained here from diagonalizing the zeroth-order Hamiltonian to running a dimer calculation and inferring from it which transitions may have LE or CT character.

4. How does addition perturb LE and CT states?

We now consider bringing our two monomers together and how this causes the zeroth-order LE and CT states to mix. To do this, we first briefly consider how addition alters two-electron integrals and the dimer Fock matrix.

Using NDO[45] and the spatial separation of monomer orbitals, we find

$$(piqj|rksl) = \delta_{pq}\delta_{rs}(pipj|rkrl), \tag{28}$$

where $\{p, q, r, s\}$ refer to arbitrary monomers from $\{n, m\}$. Although it might appear that integrals such as $(ninj|mkml)$ have to be obtained from a dimer electronic structure calculation, they can be estimated from monomer calculation and relative intermonomer geometry, as shown in Sec. III B 2 b of the supplementary material.

From Eq. (20), the perturbation to the Fock matrix in the atomic orbital basis will be, for $\mu \in \mathcal{M}$,

$$F^{(1)}_{\mu\mu} = \sum_{\lambda\in\mathcal{N}} (P_{\lambda\lambda} - Z_\lambda) V_{\mu\lambda}, \tag{29a}$$

$$F^{(1)}_{\mu\nu} = \begin{cases} 0, & \nu \in \mathcal{M}, \\ H_{\mu\nu}, & \nu \notin \mathcal{M}. \end{cases} \tag{29b}$$

There is no $-\frac{1}{2}P_{\mu\nu}V_{\mu\nu}$ term in Eq. (29) since $P_{\mu\nu} = 0$ if μ and ν are on different monomers.

For the Fock matrix in the basis of molecular orbitals, where the MOs are on the same monomer n, we use Eq. (29) to find

$$F^{(1)}_{ni,nj} = \sum_{\mu\in\mathcal{N}} C_{\mu,ni} C_{\mu,nj} \sum_{\lambda\in\mathcal{M}} (P_{\lambda\lambda} - Z_\lambda)\gamma_{\mu\lambda}. \tag{30}$$

We show in Sec. III B 2 c of the supplementary material that this can be written as the electrostatic interaction between two charge distributions, can be estimated from a multipole expansion,[134,135] and can therefore be approximated without requiring a separate calculation on the dimer. In particular, if there is zero net charge density on monomer m (as in an alternant hydrocarbon[46]), then $F^{(1)}_{ni,nj} = 0$ for all ni and nj.

If the MOs are on different monomers, Eq. (29) gives

$$F^{(1)}_{ni,mj} = -\sum_{\mu\in N}\sum_{\nu\in M} C_{\mu,ni} C_{\nu,mj} t_{\mu\nu} \tag{31a}$$

$$= -\, t_{\mu^*\nu^*} C_{\mu^*,ni} C_{\nu^*,mj}, \tag{31b}$$

where μ^* and ν^* are the atoms through which the two monomers are joined (we assume that the monomers are only joined through one atom, but this can clearly be generalized to more complex bonding geometries). The results in Eqs. (30) and (31b) mean that the perturbed Fock matrix is off-diagonal. This means that Brillouin's theorem no longer holds and that the ground state $|\Phi_0\rangle$ can mix with singly excited states (for alternant hydrocarbon dimers only with CT states), but as noted before,[64] the effect of this is likely to be small due to the large energy gap (see Sec. III A 1 of the supplementary material).

TABLE III. Properties of the LE and CT states obtained from the zeroth-order Hamiltonian, which correspond to excitations between monomer orbitals (used in this article) to those found from excitations between dimer orbitals.

Are the LE and CT states. . .	From monomer orbitals	From dimer orbitals
Orthogonal?	Yes	Not necessarily
Eigenstates of the *monomer* Fock matrix?	Yes	No
Eigenstates of the *dimer* Fock matrix?	No	Yes
A complete singly excited basis?	Yes	Sometimes
Uniquely defined, independent of orientation?	Yes	No
Determined from monomer calculation?	Yes	No
Always dark if CT?	Yes	Not necessarily

Using these results and the NDO assumptions of PPP theory, the perturbation to the CIS Hamiltonian matrix is therefore

$$\left\langle \mathrm{LE}_{ni}^{nj'} \middle| \hat{V} - \Delta E_0 \middle| \mathrm{LE}_{nk}^{nl'} \right\rangle = \delta_{ik} F^{(1)}_{nj',nl'} - \delta_{j'l'} F^{(1)}_{ni,nk}, \tag{32a}$$

$$\left\langle \mathrm{LE}_{ni}^{nj'} \middle| \hat{V} \middle| \mathrm{CT}_{nk}^{ml'} \right\rangle = F^{(1)}_{nj',ml'} \delta_{ik}, \tag{32b}$$

$$\left\langle \mathrm{LE}_{ni}^{nj'} \middle| \hat{V} \middle| \mathrm{CT}_{mk}^{nl'} \right\rangle = -F^{(1)}_{ni,mk} \delta_{j'l'}, \tag{32c}$$

$$\left\langle \mathrm{LE}_{ni}^{nj'} \middle| \hat{V} \middle| \mathrm{LE}_{mk}^{ml'} \right\rangle = 2(nj'ni|mkml'), \tag{32d}$$

$$\begin{aligned}\left\langle \mathrm{CT}_{ni}^{mj'} \middle| \hat{V} - \Delta E_0 \middle| \mathrm{CT}_{nk}^{ml'} \right\rangle = \delta_{ik} F^{(1)}_{mj',ml'} - \delta_{j'l'} F^{(1)}_{ni,nk} \\ - (mj'ml'|nkni),\end{aligned} \tag{32e}$$

$$\left\langle \mathrm{CT}_{ni}^{mj'} \middle| \hat{V} \middle| \mathrm{CT}_{mk}^{nl'} \right\rangle = 0, \tag{32f}$$

$$\left\langle \Phi_0 \middle| \hat{V} \middle| \mathrm{LE}_{ni}^{nj'} \right\rangle = F^{(1)}_{ni,nj'}, \tag{32g}$$

$$\left\langle \Phi_0 \middle| \hat{V} \middle| \mathrm{CT}_{ni}^{mj'} \right\rangle = F^{(1)}_{ni,mj'}, \tag{32h}$$

$$\begin{aligned}\langle \Phi_0 | \hat{V} | \Phi_0 \rangle &= \sum_{ni\ \mathrm{occ}} F^{(1)}_{ni,ni} + \sum_{mj\ \mathrm{occ}} F^{(1)}_{mj,mj} \\ &=: \Delta E_0.\end{aligned} \tag{32i}$$

From this, a number of results immediately follow. First, Frenkel excitations within the same monomer are perturbed by an uneven charge distribution on the other monomer.[122] CT states mix with Frenkel excitations, and from Eq. (31b), this is only through the Hückel-like $t_{\mu^* \nu^*}$ terms and not through two-electron terms, which are exactly zero within NDO but can be approximated to be zero at other levels of theory.[94,122] Although these results are derived in the context of PPP theory, similar results can be obtained at higher levels of theory.[122]

For the interaction of two Frenkel excitations on different monomers, we show in Sec. III B 2 of the supplementary material that (up to first order in the charge distribution on each monomer)

$$2(nj'ni|mkml') \simeq \frac{\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2}{r^3} - 3\frac{(\mathbf{r} \cdot \boldsymbol{\mu}_1)(\mathbf{r} \cdot \boldsymbol{\mu}_2)}{r^5}, \tag{33}$$

where $\boldsymbol{\mu}_1 =: \left\langle \Phi_0 \middle| \hat{\mu} \middle| \mathrm{LE}_{ni}^{nj'} \right\rangle$, $\boldsymbol{\mu}_2 =: \left\langle \Phi_0 \middle| \hat{\mu} \middle| \mathrm{LE}_{mk}^{ml'} \right\rangle$, $\mathbf{r}$ is the (vector) displacement between the centers of the two chromophores, and $r = |\mathbf{r}|$. The RHS of Eq. (33) is precisely the energy of interaction in Kasha's point dipole model.[81] Note that Eq. (33) is very approximate and Eq. (32d) can include dipole–quadrupole and higher terms. However, we will see that these higher-order terms can, in practice, be ignored (for the case of acenes) while still yielding qualitatively predictive results.

From Eq. (32e), the diagonal energy of a CT excitation $\left| \mathrm{CT}_{ni}^{mj'} \right\rangle$ will change by $F^{(1)}_{mj'mj'} - F^{(1)}_{nini} - J_{mj',ni}$, where $J_{mj',ni}$ is the Coulomb stabilization of an electron in orbital mj' and a hole in ni. In the supplementary material, we show that for uncharged initial ground-state chromophores, the leading order contribution from the $F^{(1)}$ terms in Eq. (32e) is at most $\mathcal{O}(r^{-2})$, but the Coulomb term is $\sim 1/r$, consistent with the stabilization of charge-transfer states given by Mott in 1938,[79] and still sometimes used as a point charge approximation.[136] Because Coulomb integrals are always positive (or zero for orbitals at infinite separation),[137] the energy of CT states is therefore usually lowered at first order. It appears that CT excitations involving different from/to monomers do not mix, but they can be mixed indirectly via Frenkel states.

We note that Kasha's exciton theory approximates Eq. (32d) by a point-dipole interaction[81] but does not consider CT states and, therefore, omits interactions, such as Eqs. (32b), (32c), (32g), and (32h). Frenkel-CT interactions similar to those in Eq. (32) have been incorporated in more advanced forms of exciton theory and to describe singlet fission phenomena.[3,41,94,122] These cases usually only consider states composed of HOMO/LUMO excitations [i.e., $i = 1$ and $j = 1$ in Eq. (32)], and here we provide a more general formulation. In addition, the formulation here shows that certain terms [such as Eq. (32f)] vanish rigorously within NDO, justifying their neglect at other levels of theory,[94,122] and that the mixing of Frenkel and CT states can be evaluated solely by considered the coefficients of the relevant orbitals on the atoms at which the monomers touch.

Finally, all terms in Eq. (32) can be estimated from monomer calculation and the relative geometry of the monomers using the results of this section and the electrostatics given in Sec. III B 2 of the supplementary material with Eqs. (32b), (32c), and (32h) known exactly. This means that when considering the results of dimerization at different geometries, the approximate effects of chromophore alteration can be determined without separate calculation for each dimer geometry. The interactions in Eq. (32) are illustrated in Fig. 4.

D. Where to dimerize?

Here, we apply the general methodology to dimerization, which can be considered a special case of addition where the two monomers are identical, such that $\hat{H}_{\mathcal{M}} = \hat{H}_{\mathcal{N}}$ and each molecular orbital on one monomer will be degenerate with a molecular orbital on another monomer.

One could consequently immediately define dimer orbitals as linear combinations of monomer orbitals, similar to the "Dimer molecular orbital linear combination of fragment molecular orbital" (DMO-LCFMO) method,[124,125] but this is not performed here as it complicates subsequent assignment of intermolecular and intramolecular transitions. This means that the monomer orbitals are not symmetry "pure" (they do not necessarily transform as an irrep of the dimer's point group), but it is possible and advantageous to symmetry-adapt the resulting excitations. Bringing together two monomers to form a dimer and analysis of the resultant spectrum have been considered before in (for example) Kasha's exciton

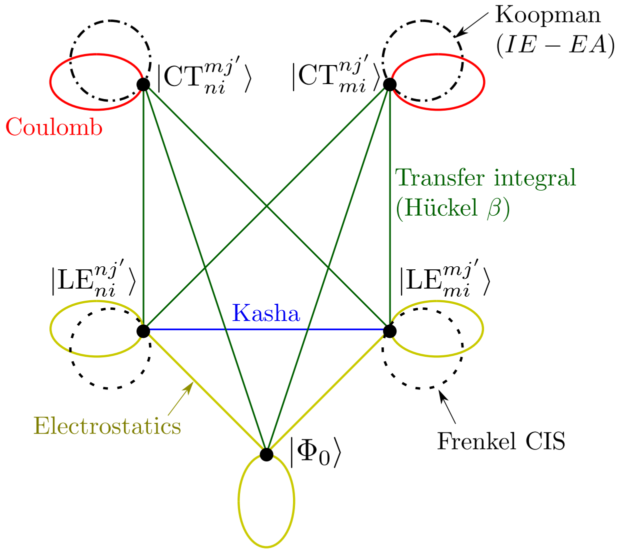

FIG. 4. Perturbation theory diagram depicting zeroth and first order interactions [Eqs. (32) and (27)], illustrating how previously-known interactions emerge naturally using the Hamiltonian definitions in this Perspective. Zeroth-order interactions [Eq. (27)] are shown as dashed lines corresponding to monomer configuration interaction singles (CIS)[1] for Frenkel excitations and Koopman's theorem (ionization energy – electron affinity)[1] for CT excitations. At first order, interactions correspond to electrostatic forces between monomers,[134,135,138] Kasha's dipole–dipole interaction,[81] Coulombic stabilization of CT excitations,[79,136] and the transfer integral (hopping term).[94] For this dimer model, there is no direct interaction between CT states going from/to different monomers at either zeroth or first order.

theory.[81] However, this only considered dipole–dipole interactions, and as we shall see, the perturbation considered here [Eq. (19)] allows for a description of a richer variety of interactions, including between two excitations where one (or both) has no transition dipole moment from the ground state.

For the case of homodimers, we immediately see that all zeroth-order eigenstates will be (at least) doubly degenerate. We, therefore, have to find the "good" eigenfunctions. This could be achieved by calculating all the mixing elements between the degenerate states, but as discussed in Sec. III A 2 of the supplementary material, group theory can often be used. For the case of a C_2 rotation interconverting the two monomers, the eigenstates will transform as A and B, letting us define

$$\left|\mathrm{LE}_k^{l',\substack{A\\B}}\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\mathrm{LE}_{nk}^{nl'}\right\rangle \pm \left|\mathrm{LE}_{mk}^{ml'}\right\rangle\right), \tag{34a}$$

$$\left|\mathrm{CT}_k^{l',\substack{A\\B}}\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\mathrm{CT}_{mk}^{nl'}\right\rangle \pm \left|\mathrm{CT}_{nk}^{ml'}\right\rangle\right), \tag{34b}$$

where LE refers to Frenkel excitation and CT refers to charge transfer. The notation is taken to mean that on the LHS, either A or B symmetry are chosen and the upper or lower sign, respectively, is taken on the RHS.

If there are further degeneracies between zeroth-order states, then linear combinations of these excitations can be taken but only within a particular irrep. Going forward, we assume that the dimer has C_2 symmetry although this methodology can easily be applied to other point groups.

To determine the effect of the perturbation between the "good" degenerate eigenstates in Eq. (34), we apply Eq. (32) to find

$$\left\langle\mathrm{LE}_i^{j',\substack{A\\B}}\middle|\hat{V}\middle|\mathrm{LE}_k^{l',\substack{A\\B}}\right\rangle = \delta_{ik}F^{(1)}_{nj',nl'} - \delta_{j'l'}F^{(1)}_{ni,nk} \pm 2(nj'ni|mkml'), \tag{35a}$$

$$\left\langle\mathrm{LE}_i^{j',\substack{A\\B}}\middle|\hat{V}\middle|\mathrm{CT}_k^{l',\substack{A\\B}}\right\rangle = F^{(1)}_{nj',ml'}\delta_{ik} \mp F^{(1)}_{ni,mk}\delta_{j'l'}, \tag{35b}$$

$$\left\langle\mathrm{CT}_i^{j',\substack{A\\B}}\middle|\hat{V}\middle|\mathrm{CT}_k^{l',\substack{A\\B}}\right\rangle = \delta_{ik}F^{(1)}_{mj',ml'} - \delta_{j'l'}F^{(1)}_{ni,nk} - (mj'ml'|nkni), \tag{35c}$$

$$\left\langle\Phi_0^A\middle|\hat{V}\middle|\mathrm{LE}_i^{j',A}\right\rangle = \sqrt{2}F^{(1)}_{ni,nj'}, \tag{35d}$$

$$\left\langle\Phi_0^A\middle|\hat{V}\middle|\mathrm{CT}_i^{j',A}\right\rangle = \sqrt{2}F^{(1)}_{ni,mj'}. \tag{35e}$$

The notation on the first three lines of Eq. (35) is taken to mean that on the LHS, either both bra and ket are A symmetry or both are B symmetry (since there is no mixing between excitations of different irreps), and the upper or lower sign, respectively, is taken on the RHS. $|\Phi_0\rangle$ is A symmetry and only interacts with A states such that ΔE_0 is the same as for addition. The CT ↔ CT mixing between A and B irreps is identical since there is no direct coupling in Eq. (32f).

Somewhat surprisingly, we find that the symmetry-adaptation of excitations leads to arguably simpler results and that the rules obtained earlier for Frenkel-CT mixing still hold for homodimers.

We note that the energy difference between two A/B Frenkel excitations is $4(nj'ni|mimj')$, which is the Davydov splitting[80] that is approximated by a point-dipole model in Kasha's exciton theory.[81]

To give an example of intensity borrowing, consider a HOMO → LUMO CT excitation borrowing intensity from a HOMO → LUMO LE. Assuming the two monomers to be joined only through one bond, we find

$$\left\langle\mathrm{LE}_1^{1',\substack{A\\B}}\middle|\hat{V}\middle|\mathrm{CT}_1^{1',\substack{A\\B}}\right\rangle = -t_{\mu^*\nu^*}\left(C_{\mu^*,n1'}C_{\nu^*,m1'} \mp C_{\mu^*,n1}C_{\nu^*,m1}\right), \tag{36}$$

and the extent of borrowing will depend on the interference between the product of orbital amplitudes at the joining carbon. If the monomer orbitals are defined such that they all have the same sign at the joining atom and the HOMO and LUMO coefficients are approximately equal on the joining atoms (which is the case for an alternant hydrocarbon[46,139]), then

$$\left\langle\mathrm{LE}_1^{1',A}\middle|\hat{V}\middle|\mathrm{CT}_1^{1',A}\right\rangle \simeq 0, \tag{37a}$$

$$\left\langle\mathrm{LE}_1^{1',B}\middle|\hat{V}\middle|\mathrm{CT}_1^{1',B}\right\rangle = -2t_{\mu^*\nu^*}C_{\mu^*,n1}C_{\nu^*,m1}. \tag{37b}$$

A similar result to Eq. (37) has previously been obtained in the context of the Davydov splitting in crystalline pentacene,[94] and here we show is a special case of Eq. (35).

The results for addition and dimerization can be summarized as follows:

Principles of chromophore design for addition and dimerization

1. CT states are always dark at zeroth-order.
2. In order for CT states to appear in the spectrum, they must (at first order) borrow from a state containing a Frenkel excitation, which differs by only one orbital from the CT excitation.
3. This Frenkel excitation must possess a dipole moment at zeroth order ($\langle \Phi_0 | \hat{\mu} | \mathrm{LE}_{mk}^{ml'} \rangle \neq 0$, which cannot be forbidden by spin symmetry or group theory using the *monomer* point group).
4. The *monomer* orbitals by which the CT and LE excitations differ must have orbital amplitude at the two atoms through which the monomers are bonded ($C_{\mu^*,mk} C_{\nu^*,ni} \neq 0$).
5. There must be a nonzero Hückel resonance term between the two joining atoms ($t_{\mu^*\nu^*} \neq 0$). Given that the overlap of two p orbitals approximately scales as $\cos(\theta)$, where θ is the dihedral angle,[103,104] this means that chromophores should be as planar as possible.

IV. TRYING IT OUT ON REAL MOLECULES

In Sec. III we have determined algebraic expressions for the mixing of states, and from this, we have determined guidelines for altering molecules such that one transition (usually a dark state at a favorable energy) borrows intensity from another transition (which must be bright and is usually at an unfavorable energy). The same perturbation theory framework can also be used to perturb the *energies* of states as well as their intensity, leading to a qualitative picture of how molecular alteration can alter the absorption and emission spectra of a molecule. Clearly, there are a huge range of possible molecular structures to which this methodology can be applied, and here, we focus on the absorption of acenes and the emission of radicals, both areas of substantial current interest from the perspective of singlet fission[3–5,95] and organic light-emitting diodes,[75,98,99,140,141] respectively. For both classes of molecules, we show how aza-substitution and addition can be used to improve their optoelectronic properties and how the methodology in this Perspective can guide where on these molecules substitution and addition should occur.

A. Visibly improving acenes

1. Background

The electronic structure of acenes has been studied since at least the 1940s[45,142,143] and is still the subject of considerable interest[6,66,74,95] due to the ability of acenes to undergo singlet fission.[3,4] These molecules generally contain a low-energy, y-polarized transition (labeled $1B_{2u}^{+}$ in Ref. 45) and an intense, high-energy x-polarized transition ($1B_{3u}^{+}$). They also possess a very weak x-polarized transition ($1B_{3u}^{-}$) between these two absorptions, which is predicted to be dark by PPP theory.

The weak visible absorption and intense UV absorption of these molecules, as shown in Table II, motivates considering whether some of the absorption intensity could be "moved" from the UV to the visible. Increasing the absorption (extinction coefficient) of these molecules in the visible would require less material in a photovoltaic device, which would, in turn, mean a thinner device such that excitons did not need to diffuse so far to be harnessed and would, therefore, increase photovoltaic efficiency.[74]

Using the foregoing design principles, in order for acenes to increase their visible absorption, the molecules must be perturbed such that transitions in the visible can "borrow intensity" from the UV absorption. Note that borrowing intensity from the pre-existing visible absorption ($1B_{2u}^{+}$), by, for example, a Kasha exciton splitting, would simply move absorption between different regions in the visible rather than increase overall visible absorption.

One idea could be to perturb the molecule such that the $1B_{2u}^{+}$ transition borrows intensity from the $1B_{3u}^{+}$. However, there is a large energy separation between these excitons, which from perturbation theory is likely to reduce their mixing, and they are orthogonal by point group symmetry such that the alteration would have to substantially reduce the molecule's symmetry in order for there to be any possibility of mixing.

Alternatively, the molecule could be altered such that the dark $1B_{3u}^{-}$ state could borrow intensity from the bright $1B_{3u}^{+}$ state. As we will show, this can be achieved by aza-substitution, which causes these excitations to mix. However, addition or dimerization of another alternant hydrocarbon (such as another acene) will *not* cause these excitations to mix, as such an alteration preserves pseudoparity, meaning that the + and − states remain orthogonal.[45]

While addition cannot cause $1B_{3u}^{-}$ to mix with $1B_{3u}^{+}$, this does not mean that addition cannot improve the spectrum: instead, addition leads to the formation of CT states, the lowest-energy of which can be in the visible and which can (subject to correct bonding geometry) borrow intensity from $1B_{3u}^{+}$. We show how the theory in this Perspective produces design rules to determine the correct geometry and compare this with experimental results.

2. Computational details

We present simulated UV/visible spectra of acenes using four methods based on the algebra in this Perspective and compare these results to experimental data. These four methods are in the order of increasing computational cost:

Methods used for the simulation of spectra

1. Zeroth-order calculation on isolated monomers,
2. algebraic first-order perturbation,
3. first-order Configuration Interaction Singles (CIS), and
4. full dimer Self-Consistent Field (SCF).

Method 1 is formally the solution to the zeroth-order Hamiltonian, which for aza-substitution involves a PPP SCF calculation on the unsubstituted molecule and for addition/dimerization involves PPP SCF calculations on the isolated monomers and subsequent CIS calculations to find the excited states. This is not expected to show any intensity borrowing but can provide a starting point for applying the TRK sum rule (see above) and indicating which state's intensity can be borrowed from and to. In method 2, the dipole moments of the zeroth-order excited states are perturbed by Eq. (8b) using the zeroth-order orbitals. This method is only slightly more computationally expensive than 1. The energies of the states are also perturbed to first order according to Eq. (10). In method 3, the first-order Fock matrix [Eq. (14) for substitution, Eqs. (30) and (31) for addition/dimerization] and first-order CIS Hamiltonian [Eq. (15a) for substitution and Eqs. (32) and (35) for addition/dimerization] are calculated using the zeroth-order orbitals. The first-order correction is added to the zeroth-order CIS Hamiltonian, and the resulting Hamiltonian is diagonalized to give the first-order excited states. This method is more computationally expensive than 2 but significantly less expensive than recalculating the two-electron integrals and the orbitals in method 4. For addition/dimerization, the two-electron integrals $(ninj|mkml)$ between monomers in Eqs. (32d) and (32e) are calculated approximately using charge distributions and the relative orientation of the monomers (as per Sec. III B 2 of the supplementary material), which is shown to be a suitable approximation in order to predict the change to the spectrum. Method 4 is a full calculation of the perturbed Hamiltonian, which is a full SCF and CIS PPP calculation run on the substituted molecule (for substitution) or dimer (for addition/dimerization). We note that for the case of aza-substitution, the ϵ_{N} (Hückel α) parameter used for method 4 is for the three-parameter model for N (where ϵ_μ and the repulsion parameters U and r_0 are changed) according to Ref. 144, whereas for perturbation theory calculations in methods 2 and 3 (where only ϵ_μ is changed), the value of ϵ_{N} is taken from Ref. 145 (see Sec. IV B of the supplementary material).

3. Aza-substitution

For the case of substitution, we, therefore, consider whether the molecule can be perturbed such that the dark $1B_{3u}^-$ transition borrows intensity from the bright $1B_{3u}^+$ transition. These transitions are both x-polarized and have different PPP pseudoparity such that they cannot mix if the molecule remains an alternant hydrocarbon.[45] However, aza-substitution breaks Coulson–Rushbrooke symmetry such that these excitations can mix.

For the case of pentacene, the $1B_{3u}^-$ and $1B_{3u}^+$ transitions are $|\Phi_{14}^-\rangle$ and $|\Phi_{14}^+\rangle$, respectively,[74] and we find

$$\langle\Phi_{14}^+|\hat{V}|\Phi_{14}^-\rangle = \sum_{v\ \mathrm{sub}} \Delta\epsilon_v (C_{v4}^2 - C_{v1}^2), \tag{38}$$

where the summation is only over the substituted atoms.

This means that in order for the excitations to mix, the acene should be substituted on the atoms that have a substantial difference in the density of orbitals 4 and 1, i.e., the HOMO − 3 and the HOMO. Inspection of the relevant orbitals[74] shows that the HOMO − 3 has a node on all long-axis (peri) carbons, whereas the HOMO has amplitude over all carbon atoms. We recall that, in general, there exists a unique pair of orbitals j (occupied) and j' (vacant) in acenes, which have a node at the long-axis positions and a constant amplitude, alternating in sign, at the short-axis positions (see Fig. 5).[45] For the case of pentacene, these orbitals correspond to orbitals 4 and 4′ (HOMO − 3 and LUMO + 3, respectively). In addition, we show in Sec. III B 4 the supplementary material that the state

$$|\Phi_1^{j',+}\rangle = \frac{1}{\sqrt{2}}\left(|\Phi_1^{j'}\rangle + |\Phi_j^{1'}\rangle\right), \tag{39}$$

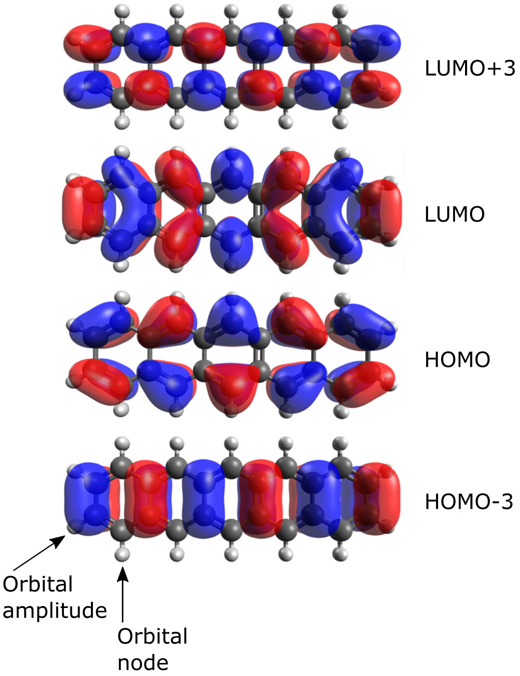

FIG. 5. The four orbitals of significance to intensity borrowing in pentacene: HOMO − 3 (bottom), HOMO, (second from bottom), LUMO (second from top), and LUMO + 3 (top) obtained from a DFT calculation. These four orbitals and their symmetry properties were described by Coulson[143] and Pariser[45] among others and are found in *all* acenes. Note, however, that the HOMO − 3 and LUMO + 3 in pentacene are *not* always the HOMO − 3 and LUMO + 3 in other acenes.

where j and j' are the unique orbitals described above, will always be x-polarized and have a significant dipole-moment, and therefore, we suggest that this always corresponds to the $1B_{3u}^+$ transition. Therefore, we expect this logic to hold for all acenes from which we suggest a general design rule:

Design rule for aza-substitution of acenes

For increased, low-energy absorption when aza-substituting acenes, place the nitrogen atoms in long-axis (peri) positions.

Aza-substitution of acenes has been considered since at least the 1960s[146] where it was noted that as the number of nitrogens increased, so did the relative height of the (originally dark) $1B_{3u}^-$ transition. This study[146] only considered substitution at the peri positions. Around the same time, research by Koutecky[48,50,147,148] presented Eq. (38) for heteroatom substitution of otherwise alternant hydrocarbons.[48] Since then, there has been a large amount of literature on aza-substituting acenes among other modifications.[146,149–159]

We compute the spectrum of TIPS-5,7,12,14-tetraazapentacene (TIPS-TAP, substitution on peri positions) at all four levels of theory where we can clearly see a new absorption emerge around 420 in broad agreement with experimental results.[149] We then consider the case of substitution at the short-axis (cata) positions where we observe, as predicted by theory and experiment,[153,154] that no significant new low-energy absorption appears in the spectrum. These results are presented in Fig. 6. Although the algebraic perturbation and first order methods have quantitative differences in spectra from the full SCF calculation, namely, that the perturbation theory methods exaggerate the intensity of the new absorption, in all three cases, they capture the essential photophysics: a new absorption upon substitution at long-axis positions. A very small new absorption is seen upon substitution at short-axis positions, which is replicated by perturbation theory, but this does not significantly change the spectrum.

4. Addition and dimerization

Similar to the case of aza-substitution, here we consider how addition and dimerization of acenes can increase their low-energy absorption intensity. Provided that the molecule being added to the starting monomer is also alternant, then the dimer/oligomer will also be alternant, and PPP psuedoparity will be preserved. This means that for this type of modification, it will not be possible to mix "plus" and "minus" states in the same, as discussed earlier for aza-substitution.

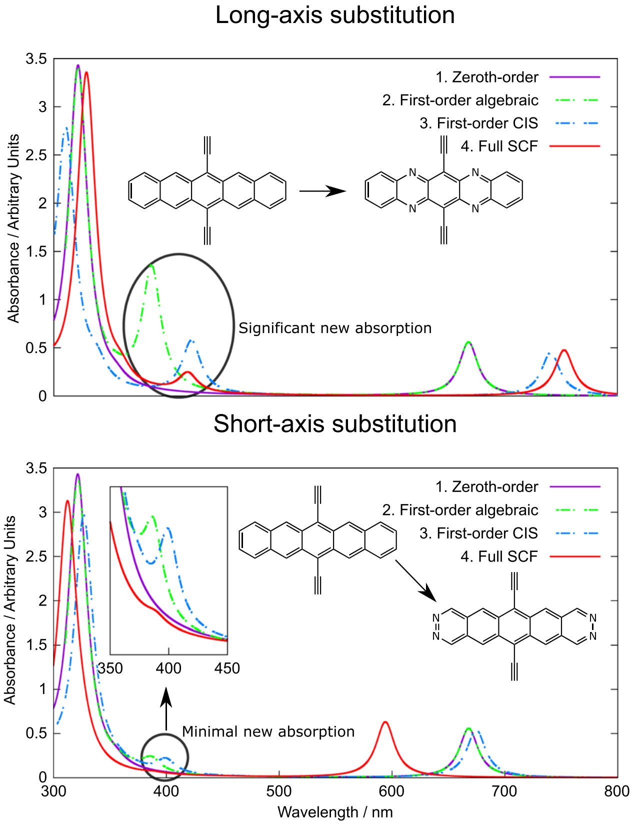

FIG. 6. Intensity borrowing upon tetra-aza-substitution of TIPS-pentacene at long-axis positions (top) and short-axis positions (bottom). The unsubstituted TIPS-pentacene spectrum is shown as "Zeroth Order" along with predicted spectra of (i) TIPS-5,7,12,14-tetraazapentacene (TIPS-TAP) (top) and (ii) TIPS-2,3,9,10-tetraazapentacene (bottom) at varying levels of theory. A new absorption can be seen around 430 nm after aza-substitution at the 5, 7, 12, and 14 positions as clearly shown by calculations at all levels of theory (top). Only a small new absorption can be seen after aza-substitution at the 2, 3, 9, and 10 positions (bottom).

Nevertheless, upon dimerizing, it may be possible for the HOMO to LUMO CT excitation (suitably symmetry adapted) to borrow intensity from the intense UV peak. As we have shown previously[74] for the case of pentacene dimers, the mixing of the HOMO–LUMO CT excitation and the high-energy UV absorption is

$$\left\langle \Psi_0 \middle| \hat{\mu} \middle| \mathrm{CT}_{11}^{B,(1)} \right\rangle = -\langle \Psi_0 | \hat{\mu} | \mathrm{LE}_{14}^{+,B} \rangle \frac{\sqrt{2} t_{v^*\sigma^*} C_{v^*,n1} C_{\sigma^*,m4}}{E(\mathrm{CT}_{11}^{B}) - E(\mathrm{LE}_{14}^{+,B})}, \tag{40}$$

where v^* and σ^* are the atoms through which the dimer is bonded, $t_{v^*\sigma^*}$ is the relevant hopping term, $C_{v^*,n1}$ is the HOMO coefficient of atom v^* on monomer n, and $C_{\sigma^*,m4}$ is the HOMO − 3 coefficient on monomer m. As described above in Sec. IV A 3 and in more detail in Sec. III B 4 of the supplementary material, the same reasoning can be applied to all acenes,[45,74] which leads to a simple design rule for increased low-energy absorption:[74]

Design rule for addition/dimerization of acenes
For a new, intense low-energy absorption in acene dimers, join via a short-axis (cata) carbon atom.

This can also be extended using symmetry arguments[74] that there should be no long-axis symmetry plane through adjacent monomers. We illustrate this design rule computationally with application to two pentacene 2,2′- dimers: pentacene-tetracene 2,2′-dimer and pentacene 2,2′-homodimer whose spectra are presented in Figs. 7 and 8.

In both cases, a new, low-energy absorption is seen in accordance with experimental findings.[31,74] The energy of this new absorption in the experimental data are well reproduced by full SCF calculation (method 4) but also by all approximate methods above zeroth-order; however, it is difficult to compare the intensities of the experimental spectra with those of the simulated spectra. When comparing the approximate models to the full calculation in method 4, the intensity of the new absorption is predicted most accurately for method 2, which predicts the highest intensity for all four dimers, but method 3 reproduces the energies of the new absorption most accurately when compared to method 4. In the supplementary material, we present the corresponding spectra for the 1,1′-analogs, none of which show a new low-energy absorption in accordance with our theory and whose simulated spectra at all levels of theory are almost identical. We also present the spectra of pentacene–anthracene and pentacene–hexacene 2,2′ dimers in the supplementary material. Although the algebraic first-order perturbation 2 and first-order Hamiltonian diagonalization method 3 have slight numerical differences in the energies and intensities when compared to the full calculation, they capture the qualitative change in the spectra upon dimerization: a new absorption upon dimerization at the 2,2′- positions but no new absorption upon dimerization at the 1,1′- positions. This confirms the use of the methodology presented in this Perspective for spectral prediction and molecular design.

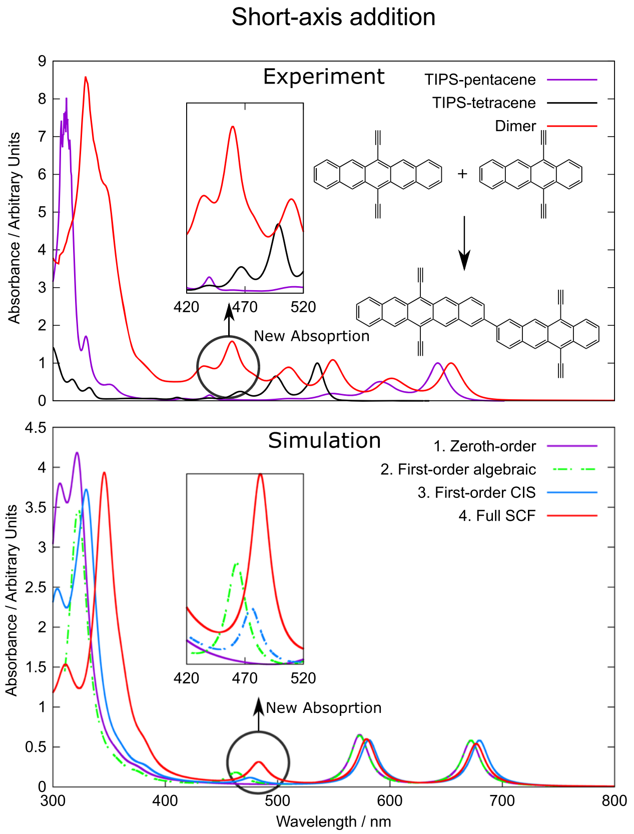

FIG. 7. Simulated UV/visible spectrum of TIPS-2,2′-pentacene–tetracene (bottom) from PPP-SCF/CIS and intensity-borrowing perturbation theory calculations along with the experimental spectra of the dimer the monomers (top). A new absorption is seen around 460 nm in the experimental spectrum, predicted by our calculations to be between 460 and 485 nm and seen at all levels of theory above zeroth order.

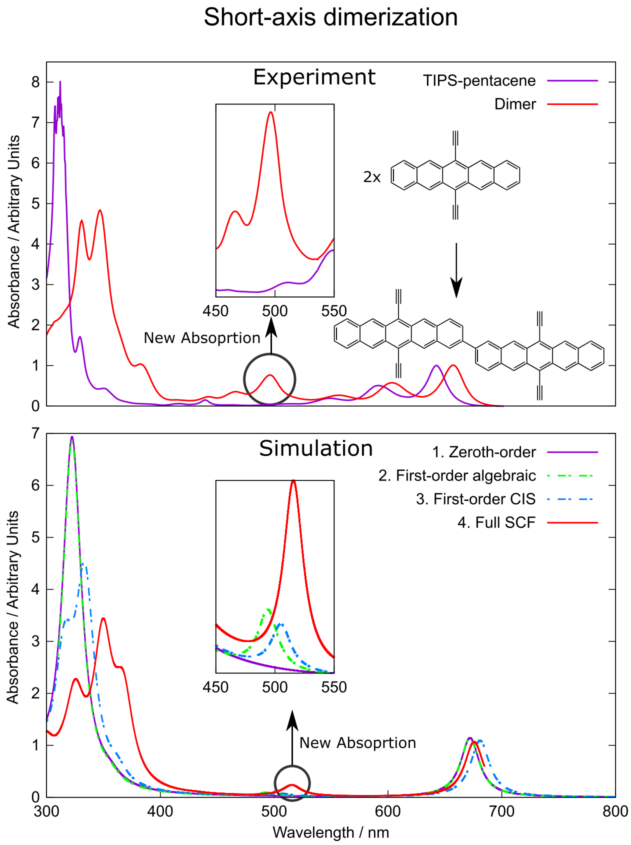

FIG. 8. Simulated UV/visible spectrum of TIPS-2,2′-bipentacene (bottom) from PPP-SCF/CIS and intensity-borrowing perturbation theory calculations along with the experimental spectra of the dimer and monomer (top). A new absorption is seen around 500 nm in the experimental spectrum, predicted by our calculations to be between 490 and 520 nm and seen at all levels of theory above zeroth order.

B. Brightening dark radicals

Here, we show how the design methodology given in Perspective article can and has been applied to design highly efficient and emissive radical-based organic light-emitting diodes.[75,98] This area has already been extensively reviewed from an organic chemistry[141] and applied physics perspective[75] and been the subject of numerous experimental,[75,98,160] computational,[160–164] and theoretical[140] studies, and here we consider the problem from an inverse design perspective.

1. To emit or not to emit

Stable organic radicals have been known since 1900 with the discovery of the triphenylmethyl (TPM) radical.[141] Various other stable organic radicals have also been known for some time, such as the phenalenyl radical and TEMPO.[141] However, these radicals are not emissive. Attempts were made to stabilize and alter organic radicals, such as by chlorination of the TPM radical, leading to TTM and PTM radicals,[141] which were also not emissive. Further phenyl groups were bonded to the TPM radical,[165] leading to derivatives with very weak D_1 (lowest excited doublet) absorption. Since the rate of spontaneous emission (fluorescence) is proportional to the absorption for that transition,[2] these investigations led to the belief that no stable radicals were fluorescent.[141,166]

It was then noticed, somewhat surprisingly, that carbazole-, triarylamine-, and other aza-derivatives of the TTM radical could, in fact, be emissive in the red and near-infrared regions of the spectrum.[167–169] In a further development in 2015, Peng *et al.* demonstrated an emissive radical in a functioning OLED based on TTM-1Cz [(4-N-carbazolyl-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical].[170] Even more surprisingly, in 2018, Ai *et al.* announced a radical OLED, which was 27% efficient at 710 nm, believed to be the highest efficiency of any known LED in that region of the spectrum, and based on the TTM-3NCz [tris-(2,4,6-trichlorophenyl)methyl 3-substituted-9-(naphthalen-2-yl)-9H-carbazole] molecule.[98]

These discoveries seemed particularly surprising, given that the emissive radicals were derivatives of the non-emissive triphenylmethyl radical and that previous attempts to functionalize the triphenylmethyl radical had resulted in non-emissive molecules. Since 2018, numerous other emissive radicals have also been reported.[99,141]

In 2020, it was shown (be rediscovering algebraic theory from the 1950s[171–173] and applying it to OLED emission) that if the radical is an alternant hydrocarbon (i.e., it only has even membered rings and no heteroatoms within the conjugated structure), then it will have a vanishingly small transition dipole moment for the $D_1 \rightarrow D_0$ transition, meaning that the radiative rate will be slow and usually outcompeted by non-radiative decay.[75] This, therefore, led to a simple design rule for emissive radical OLEDs:

Major design rule for light-emitting radicals
The emitter must not be an alternant hydrocarbon

A comparison of emissive and non-emissive triphenylmethyl radical derivatives[99] corroborated these theoretical results in finding that all emissive radicals were non-alternant and that the non-emissive derivatives of the triphenylmethyl radical were all alternant.

In the language of machine learning, what had happened (most likely unintentionally) was that the morphing operations applied to the TPM radical kept it within the space of alternant hydrocarbons, and molecular structures that could be shown on theoretical grounds would be extremely unlikely to emit. This led to the erroneous belief that there were no stable emissive organic radicals[166] and arguably delayed progress in the field. We believe that this highlights the importance of determining whether or not the proposed morphing operations can ever lead to the properties that are desired from the molecule (in this case, what alterations to the TPM radical could cause it to have a significant $D_1 \rightarrow D_0$ transition dipole moment and, therefore, be emissive).

The rediscovery of algebraic expressions for radical absorption[75] explained that organic radicals must not be alternant in order to emit but did not give a clear prescription as how this should best be achieved. Alternant hydrocarbon radicals usually have a dark D_1 state, which is[140,173]

$$|D_1\rangle \simeq \left|\Phi_{10}^{-}\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\Phi_{\bar{1}}^{\bar{0}}\right\rangle - \left|\Phi_{0}^{1'}\right\rangle\right), \tag{41}$$

that is, an out-of-phase combination of HOMO to SOMO and SOMO to LUMO excitations, which has a vanishing dipole moment. Conversely, the plus combination

$$\left|\Phi_{10}^{+}\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\Phi_{\bar{1}}^{\bar{0}}\right\rangle + \left|\Phi_{0}^{1'}\right\rangle\right) \tag{42}$$

usually has a substantial transition dipole moment.[173]

In practice, there are two ways of forming a bright D_1 state: aza-substituting the radical, which causes $\left|\Phi_{10}^{-}\right\rangle$ to mix with $\left|\Phi_{10}^{+}\right\rangle$ and borrow intensity from it, or addition of a non-alternant donor group, which leads to a low-energy donor-HOMO to radical-SOMO excitation (beneath $\left|\Phi_{10}^{-}\right\rangle$ in energy), which can then borrow intensity from $\left|\Phi_{10}^{+}\right\rangle$. Note that adding a donor group that is alternant to the radical does does not increase emission but simply leads to a lower-lying dark state.[99]

2. Aza-substitution

Aza substitution breaks PPP pseudoparity and causes the originally dark $\left|\Phi_{10}^{-}\right\rangle$ D_1 state to borrow intensity from the bright $\left|\Phi_{10}^{+}\right\rangle$ state,

$$\left\langle\Phi_{10}^{+}\middle|\hat{V}\middle|\Phi_{10}^{-}\right\rangle = \sum_{v\ \text{sub}} \Delta\epsilon\left(|C_{0v}|^2 - |C_{1v}|^2\right), \tag{43a}$$

$$\therefore \left\langle\Phi_0\middle|\hat{\mu}\middle|D_1^{(1)}\right\rangle \simeq \langle\Phi_0|\hat{\mu}|\Phi_{10}^{+}\rangle \frac{\sum_{v\ \text{sub}}\Delta\epsilon\left(|C_{0v}|^2 - |C_{1v}|^2\right)}{E(\Phi_{10}^{-}) - E(\Phi_{10}^{+})}. \tag{43b}$$

This suggests that the radical should be substituted on atoms whose HOMO and SOMO coefficients differ significantly in magnitude. To our knowledge, TTM has been aza-substituted at the para position to make PyBTM[99] but not at the meta position where there is vanishing SOMO amplitude.[98] We suggest that this may lead to brighter radicals.

Aza-substitution can also be used to blue-shift emission of a donor–acceptor molecule.[75] While formation of the donor–acceptor species can be described using the framework in this Perspective for addition (see Sec. IV B 3), the effect of aza-substitution on the donor–acceptor species can be described using the substitution algebra. We denote the acceptor (TTM) as monomer n and the donor (usually Carbazole or a derivative thereof) to be m. Approximating the D_1 state as $\left|\mathrm{CT}_{m1}^{n0,(1)}\right\rangle$, aza-substituting the donor perturbs the donor HOMO energy by

$$\Delta E = \Delta\epsilon \sum_{v\text{sub}} C_{vm1}^2 \tag{44}$$

as $\Delta\epsilon < 0$ for nitrogen (due to its higher electronegativity than carbon); this lowers the energy of the donor HOMO and thereby increases the energy of the $\left|\mathrm{CT}_{m1}^{n0,(1)}\right\rangle$transition. This has been applied successfully to blue-shift emission of TTM-1Cz from 687 nm to 612–643 nm depending on the location of the substitution.[75] Furthermore, the extent of blue shifting can be predicted approximately by inspection of the donor HOMO orbitals: the larger the HOMO coefficient on a given atom, the greater the likely blueshift. In practice,[75] this is only a qualitative guide, since the shape of the donor orbitals changes upon aza-substitution, and a more reliable predictor of blue-shifting can be obtained from the energies of the HOMOs of the aza-substituted donor (which is still substantially computationally cheaper than an excited-state calculation on the full radical).

3. Addition

For addition, to break the alternacy symmetry, a non-alternant moiety (usually an electron-rich donor group) is bonded to the TTM group (knows as the acceptor).[99] This leads to a charge-transfer excitation $\left|\mathrm{CT}_{m1}^{n0}\right\rangle$, which is (or rather, can be) beneath the energy of the dark $\left|\mathrm{LE}_{n1n0}^{-}\right\rangle$ state of TTM. However, as discussed earlier, to a first approximation, CT states are themselves dark such that *prima facie* this process simply leads to a different dark D_1 state. However, it is possible for this state to borrow intensity from the intense $\left|\Phi^{+}_{n1n0}\right\rangle$ state of TTM,[75,140]

$$\left\langle\Phi_0\middle|\hat{\mu}\middle|\mathrm{CT}^{n0,(1)}_{m1}\right\rangle \simeq -\frac{1}{\sqrt{2}}\left\langle\Phi_0\middle|\hat{\mu}\middle|\mathrm{LE}^{+}_{n1n0}\right\rangle \times \frac{t_{\nu^*\rho^*}C_{n1,\nu^*}C_{m1,\rho^*}\ \cos(\theta)}{E(\mathrm{CT}^{n0,(0)}_{m1}) - E(\mathrm{LE}^{+}_{n1n0})}, \qquad (45)$$

where the monomers are joined through atoms ν^* and ρ^* with dihedral angle θ. This can be summarized as a design rule:[75]

Design rule for light-emitting radicals by addition
There must be substantial orbital amplitudes on the radical HOMO and donor HOMO on the atoms by which they are joined.

This is found to hold experimentally in emissive donor–acceptor radicals.[75]

C. Different molecules, similar rules

This section on radicals has considered two very different motivations for tailoring spectra: increasing absorption in the visible (not necessarily of the S_1 absorption) for photovoltaics and singlet fission and increasing emission from the D_1 state of radical organic light-emitting diodes. Although seemingly very different goals, the algebraic expressions for aza-substitution [Eqs. (38) and (43)] and addition [Eqs. (40) and (45)], in both cases, are algebraically similar. This illustrates how the theoretical formalism of this article can be applied without substantial modification to a wide variety of problems.

The numerical examples given in this Perspective clearly show that the theoretical methodology can make the correct qualitative predictions for spectral changes upon molecular substitution, addition, and dimerization. However, there can be occasions where this could break down. One is for accidental degeneracies where the perturbation to the zeroth-order states is not small and perturbation theory itself breaks down. In this case, quasidegenerate perturbation theory can be used. Another case could be if the orbitals of the altered chromophore are substantially different to the orbitals of the unaltered chromophore such that perturbing excitations only (not orbitals) may be insufficient. One possible example of this is 6,6′-bipentacene, which is explored in Sec. IV B 3 of the supplementary material.

V. TO CONCLUDE

We can summarize the results of this Perspective into the three major principles of chromophore design given in the Introduction.

Results similar to these have previously been obtained in very different contexts and, here, we show that they can be obtained within a consistent theoretical framework. The conservation of oscillator strength, principle 1, is an adaptation of the textbook Thomas–Reiche–Kuhn sum rule.[2] Excitations mix upon substitution if and only if they differ by one orbital, and the orbitals by which the excitations differ having amplitude on the substituted atom, principle 2, have been obtained algebraically in the context of transition polarizations in aza-substituted acenes.[50]

The form of the zeroth-order Hamiltonian in principle 3 has been used in (for example) simulating polymer–fullerene blends,[174] and similar LE and CT definitions in principle 3a appear in a DFT exciton model.[122] CT states acquiring intensity by mixing between excitations in principle 3b has already been shown for acene dimers[74] and is consistent with (for example) Mulliken's theory of charge-transfer spectra[127,128] (see Sec. IV B 3 of the supplementary material), and Coulombic stabilization of a CT excitation dates from the 1930s.[79] Here, we also show that it is approximately a charge-dipole term if the two excitations differ by one orbital and a dipole–dipole term if they differ by two orbitals. LE/CT mixing through one-electron terms in principle 3c is commonly used for discussing HOMO/LUMO interactions in singlet fission,[94,175] and here we show how it can extend to general excitations and be determined from examining orbital coefficients on the joining atoms. Mixing between LE states in principle 3d builds upon Kasha exciton theory,[81] though the LE/LE interaction derived here operates between different (bright) LEs and not solely between the same LE on each monomer as in the original formulation.[81]

The results given here are independent of the molecule considered, provided its chromophore is satisfactorily described by a π system and, therefore, by the PPP model. They also do not require presumption of a specific parameterization scheme for PPP or for the hydrocarbon to be alternant.[139]

In future work, we propose extending this methodology to dimerization via a linker or "wire," which has been the subject of recent experimental and theoretical studies.[95,123] By consideration of the ground state mixing of CT excitations through Mülliken's theory[127,128] and of double and higher excitations, we could extend our methodology to a wider variety of charge-transfer dimers and complexes. The dimerization methodology can be extended further to oligomers and polymers, and a combination of different alterations considered to observe their combined effect. From a theoretical viewpoint, there is the possibility of extending this analysis to other observables using an operator other than the dipole moment in the perturbation expression [Eq. (8b)].

As already discussed, some of the design rules in this Perspective, such as for acene dimer absorption[74] and efficient radical emission,[75] have already been published in conjunction with experimental results. It is our hope that the methodology in this Perspective can guide synthetic efforts in the future.

We also hope that these findings may be implemented in artificial intelligence calculations, such as machine learning or genetic algorithms, in order to bias morphing operations in favor of those with a greater likelihood of achieving the desired spectral alteration, increasing the rate of molecular discovery, and enabling inverse molecular design.

SUPPLEMENTARY MATERIAL

The supplementary material contains additional flow diagrams for molecular design methodology, additional data for typical chromophores, further background theory, implementation details, additional figures, computational details and parameterization, and atomic co-ordinates of the simulated chromophores.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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