

Transition Moment Vector Alignment – A Qualitative Approach for the Rational Design of Intensely Colored Organic Compounds

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Abstract

The hypothesis of vector alignment may assist the rational design of intensely colored conjugated organic dyes by providing a means of predicting the structures that provide a straight path for the π electrons to move across the entire molecule in response to perturbation by a passing photon.

Keywords: Transition moment vector, transition dipole moment, alignment, organic synthesis, conjugation, pi-system, color, dye

Introduction

The growth of worldwide demand for inexpensive solar energy, which drives the demand for dye-sensitized solar cells (DSSCs), creates a need for strongly absorbing organic dyes. Since only a single layer of dye molecules coats the semiconductor in the DSSC,¹ it is imperative that each dye molecule be as efficient a photon trap as possible. More efficient dyes will also have other important applications. Certain dyes that strongly absorb electromagnetic radiation will efficiently produce singlet oxygen (assuming the other relevant processes², including intersystem crossing to the triplet state, diffusion of oxygen to and from the excited dye and energy transfer to ground-state triplet oxygen, are all efficient). Such dyes would be important in photodynamic cancer therapy. Strongly absorbing molecules may assist the production of cheaper inks, as the same perceived color intensity could be produced with smaller quantities of dye.

The transition moment vector (TMVs) can be explained as chromophores with 2-fold symmetry or no plane of symmetry other than the plane of the π -system (for example, naphthalene, perylene, or quinoline) have a preferred direction relative to the molecular framework in which the electron density is most easily redistributed by the electric vector of an interacting photon. This preferred direction is called a transition moment vector.³ This redistribution of electron density creates a transient dipole, and for this reason the TMV concept is also referred to as transition dipole moment.⁴ Each electronic transition (*e.g.*, ground state to lowest excited singlet, S_0 - S_1 ; ground state to second excited singlet, S_0 - S_2 ; etc.) has its own TMV,⁵ and the directions of each TMV are often different.

The schematic illustration of vector alignment is depicted in Figure 1. Two chromophores can be attached in one of three ways: the two vectors may be a) collinear, b)

parallel but not collinear, and c) angular. *The vector alignment hypothesis predicts that bichromophoric molecules consisting of a collinear TMV arrangement will produce the molecules bearing the strongest chromophore among the three possibilities.*

In the present discussion, the TMV is meant to be that of the lowest energy singlet-to-singlet transition (HOMO-LUMO), unless otherwise stated.⁶ The TMV can be more accurately described as the dipole induced by the electric field of a photon in a quantum mechanical system, i.e., the projection of the perturbed ground state wavefunction Ψ_a onto higher energy excited-state wavefunction Ψ_b by a photon. The probability of the photon being absorbed is highest if the photon's energy equals the energy difference between Ψ_a and Ψ_b ; the operator μ describes this absorption.⁷ Thus for the purposes of this discussion the TMV will be referred to as μ -operator.

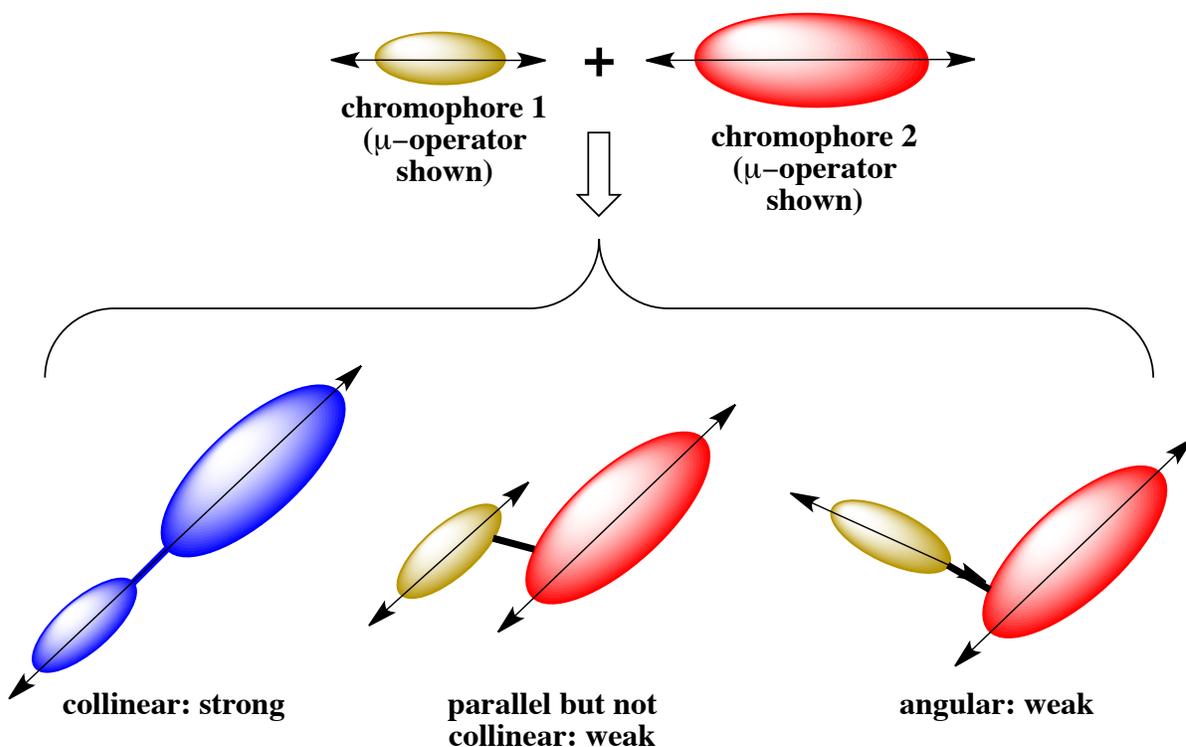


Figure 1. The three possible arrangements of two chromophores in a bichromophoric molecule (the double-headed arrow shows the direction of μ -operators of each chromophore)

The orientations of relative μ -operators to their parent molecules have been experimentally determined by placing the molecule of interest in anisotropic surroundings, such as stretched polymer films,⁸ crystals,⁹ or cyclodextrins,^{5a} which serve to orient the molecule of interest relative to its immediate environment or to the spectrometer.

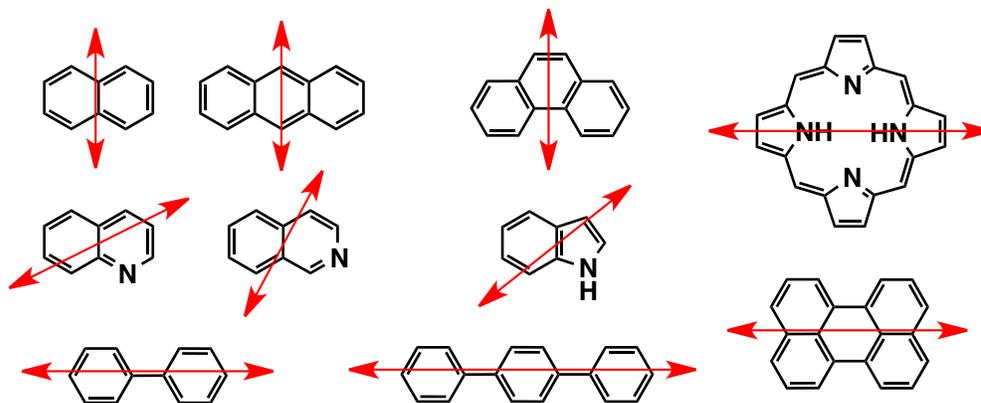


Figure 2. Selected examples of experimentally determined transition moment vectors (μ -operators) and their directions (red double-headed arrows) relative to the structure of the molecule

Several examples of experimentally determined μ -operators are shown in Figure 2¹⁰ (the magnitudes of the μ -operators were not reported). All the shown μ -operators (red double-headed arrows) are for the lowest energy transition, which may be parallel to either the length (*e.g.*, biphenyl) or the width (*e.g.*, naphthalene), or bear no apparent correlation to the structure (*e.g.*, indole).

New terminology

The new parameter, antenna quality (AQ), is hereby defined to be used to measure the results of vector alignment. Antenna quality is calculated according to following equation where the molar extinction coefficient (ϵ) and λ_{\max} are in $\text{Lmol}^{-1}\text{cm}^{-1}$ and nm, respectively, p is the number of π electrons involved in the chromophore, and 10^7 nm cm^{-1} is a units conversion factor:

$$AQ = \frac{\epsilon \lambda_{\max}}{10^7 p}$$

The antenna quality is directly proportional to the strength of the chromophore for a given number of π electrons (the higher the antenna quality is, the stronger the chromophore). The values of AQs have the advantages of allowing chromophores of different sizes to be directly compared and of being easily available from published UV-visible absorption data. A total of 260 AQs were calculated from published data.¹¹ From these calculations, it was found that the majority (190) fell in the numerical range of 0.1 to 0.01. In this study, AQs of 91 compounds were calculated; 70 of them fell in this range (77%), 13 were above (14%), and eight below (9%).

The use of oscillator strength for measurement of the results of vector alignment was found to be unsatisfactory. Oscillator strength of a transition between state i and state j is determined experimentally by integration of the absorption peak in the UV-visible spectrum as described by the following equation.⁴

$$f_{ij} = (k/n) \int \epsilon(\lambda) d\lambda$$

In this equation $\epsilon(\lambda)$ is the molar absorption coefficient as a function of wavelength (λ); n is the refractive index of the medium; and k is a unit-converting constant with the value of $4.32 \times 10^{-9} \text{ cm} \cdot \text{mol} \cdot \text{L}^{-1}$.

Calculation of oscillator strength requires measuring the extinction coefficients at many wavelengths, and using this data to calculate a definite integral (Note: according to the definition, oscillator strength is a definite integral, despite the indefinite integral shown). Often only the λ_{max} and its accompanying ϵ are given, particularly in the older literature. Furthermore, computation of a definite integral requires that the endpoints of the integration be located, and even if extinction coefficients at many wavelengths are available, the location of these endpoints may be ambiguous in the spectrum. However, the area under an absorption peak could be calculated from a number of AQs taken at evenly spaced intervals across the peak of interest.

The effects of vector alignment can be seen by comparing the AQs, derived from the UV-visible spectra, of isomeric conjugated molecules that have more than one chromophore. It should be noted that for some of the molecules discussed here, the molar extinction coefficients (ϵ) were not explicitly stated in literature but graphs of the absorption spectra were supplied, from which the extinction coefficients could be estimated. However, the differences in AQs were readily apparent despite the errors associated with the estimations.

The vector alignment hypothesis predicts that the compounds with the highest AQs obtainable from a given set of chromophores will be obtained by assembling the constituent chromophores in such a way that all the μ -operators are either collinear or as close to collinear as possible. Collinear μ -operators (the ideal arrangement) are expected to give a straight path for electron density to follow in response to perturbation by a photon. Any deviations from a linear path are predicted to cause the AQ to be less than the optimum.

While interactions of μ -operators have been previously mentioned in the literature,^{12,13,14} intramolecular vector alignment does not appear to have been addressed as a widely applicable concept for the design of molecules with strong chromophores. The following discussion addresses this inadequacy in the literature.

Discussion: Examination of Literature Data for Evidence for Vector Alignment

Bisbenzothiophenes: Between two isomeric bisbenzothiophenes **1** and **2** (Figure 3), the S,S,S-*anti,anti*-isomer **2** has a much higher AQ than its S,S,S-*syn,syn*-counterpart **1** (Table 1).¹⁵ The results are in good agreement with the TMV hypothesis because the two lowest energy μ -operators of **2** are in a near collinear arrangement compared to those in **1** (Figure 3).



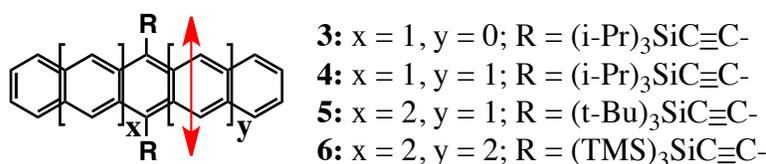
Figure 3. Two isomers of thieno[*f,f'*]bis[1]benzothiophene

Table 1. Comparison of the spectrophotometric data of thieno[*f,f'*]bis[1]benzothiophenes

Compound	λ_{\max} (nm) ^a	$\log \epsilon^a$	p	AQ ×100
1	363	3.00	22	0.165
2	375	3.74	22	0.937

^aThe values of λ_{\max} and ϵ were recorded in dichloromethane.¹⁵

Acenes vs. Rylenes: The μ -operators for naphthalene and anthracene are perpendicular to the long axis of the molecule (Figure 2). Based on that, it is assumed in present study that adding more fused-benzene rings to either end of the acene structure does not change the orientation of the μ -operator (Figure 4). In addition, the chromophore propagation of the system is parallel but not collinear. The AQs were calculated from the UV-visible data available for the four diacetylene-acenes,^{16,17} which were tabulated in Table 2.

**Figure 4.** General formula representing selected series of acenes**Table 2.** Comparison of the spectrophotometric data of acenes

Cmpd	x, y	R	λ_{\max} (nm) ^a	$\log \epsilon^a$	p	AQ ×100
3	1, 0	$(i\text{-Pr})_3\text{Si}-\text{C}\equiv\text{C}-$	535 ^b	4.42 ^b	22	6.40
4	1, 1	$(i\text{-Pr})_3\text{Si}-\text{C}\equiv\text{C}-$	643	4.30	26	4.95
5	2, 1	$(t\text{-Bu})_3\text{Si}-\text{C}\equiv\text{C}-$	734	4.12	30	3.25
6	2, 2	$(\text{TMS})_3\text{Si}-\text{C}\equiv\text{C}-$	851	4.11	34	3.23

^aThe values of λ_{\max} and ϵ were recorded in dichloromethane unless otherwise noted.¹⁶ ^bThe values were recorded in hexanes.¹⁷

Unlike in the acene series, μ -operators of rylenes propagate collinearly with the addition of each naphthalene group (Figure 5). Thus, a steady increase of AQs with each chromophore addition is expected. For proper comparison among rylenes **7-11**,¹⁸ the data for the higher rylene analogues **10** and **11** have been derived from those of **10a** and **11a** by removing the influence of electron donation from the solubilizing R_2 groups (Figure 5). Since only the λ_{\max} of **10** (831 nm) can be found in the literature without its molar extinction coefficient, the AQ for **10** was estimated using the ϵ value of relevant **10a** ($R_2 = 4\text{-}(2,4,4\text{-trimethylpent-2-yl})\text{phenoxy}$). Similarly, the AQ for rylene **11** was estimated by using the relevant values that were published for related **10a** ($\lambda_{\max} = 877$ nm) and **11a** ($\lambda_{\max} = 953$ nm, $\log \epsilon$ 5.47). Thus, the λ_{\max} for **11** is estimated at 907 nm ($907 = 953 - (877 - 831)$) and its $\log \epsilon$ is assumed as 5.47 (Table 3).

Despite these adjustments, the data in Tables 2 and 3 bear out the predictions. The AQs of the rylenes showed a sharp increase with increasing molecular length (increasing n), in good agreement with the hypothesis (collinear addition). On the other hand, the acene series exhibited a steady *decrease* in AQs despite increasing molecular length.

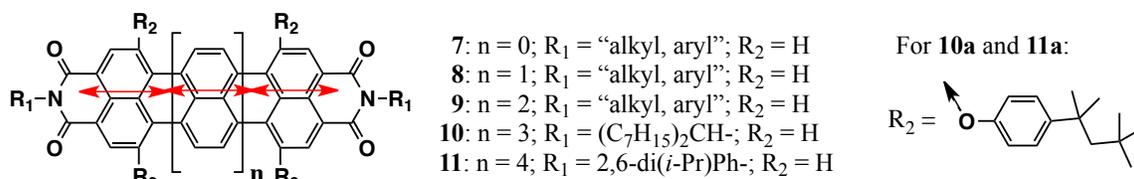


Figure 5. General formula representing selected series of rylene (R_1 groups for 7-9 were not specified)

Table 3. Comparison of the spectrophotometric data of rylene

Cmpd	n	R_1	R_2	λ_{\max} (nm) ^a	$\log \epsilon^a$	p	AQ $\times 100$
7	0	"alkyl, aryl"	H	580	4.66	32	8.28
8	1	"alkyl, aryl"	H	680	4.96	42	14.8
9	2	"alkyl, aryl"	H	780	5.24	52	26.1
10	3	$(\text{C}_7\text{H}_{15})_2\text{CH}$	H	831	5.37	62	31.9
11	4	2,6-di(<i>i</i> -Pr)Ph	H	907	5.47	72	37.2

^aThe values of λ_{\max} and ϵ were recorded in chloroform.¹⁸

Porphyrins: The μ -operator alignment of the porphyrin core is depicted in Figure 2. For the related compounds **12** and **13**, two possible orientations of μ -operators shown in red and blue arrows can be drawn (Figure 6).¹⁹ For compound **13** the blue set of vectors (shown also as hollow arrows) comes much closer than the red set to being collinear. In the similar trend, the blue vector set of **13** is also more collinear than both red and blue vector sets of **12** (Figure 6). The vector alignment hypothesis predicts that because compound **13** has vectors that are closer to collinear than those in **12**, the AQ of **13** will be higher than that of **12**. The data in Table 4 confirms this expectation (**13/12** AQ ratio > 6) and agrees with the hypothesis.

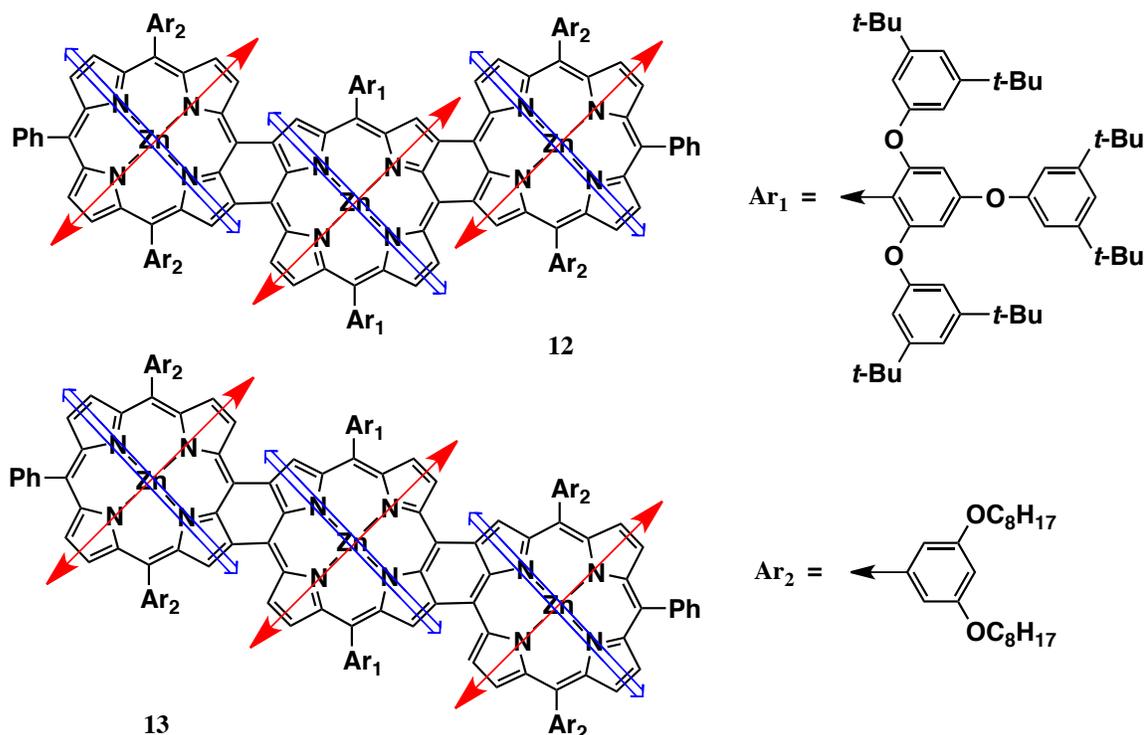


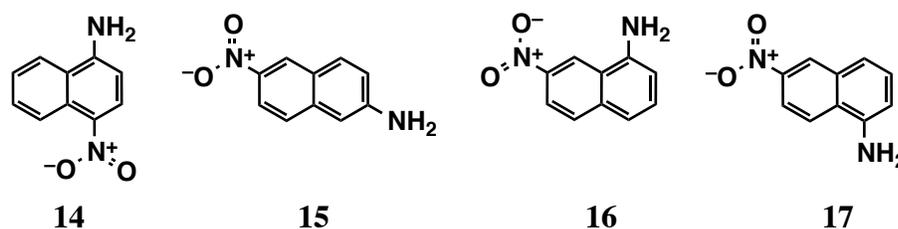
Figure 6. Rigid metallated triporphyrins with solubilizing groups

Table 4. Comparison of the spectrophotometric data of rigid triporphyrins

Compound	λ_{\max} (nm) ^a	log ϵ ^a	p	AQ \times 100
12	982	4.35	78	2.82
13	963	5.18	78	18.7

^aThe values of λ_{\max} and ϵ were recorded in chloroform.²⁰

Vector Augmentation: Closely related to vector alignment as described above, is the practice of putting auxochromes or small unsaturated groups on a fragment possessing a μ -operator with a well-defined direction. This could be called vector augmentation. An example of this series is provided by the amino-nitro-naphthalene derivatives in Figure 7. According to the data in Table 5,²¹ compound 14 gives the strongest chromophore, as would be expected from the position of the μ -operator in naphthalene and the attachments of functional groups in the same direction.

**Figure 7.** Naphthalene derivatives for vector augmentation study**Table 5.** Comparison of the spectrophotometric data of naphthalene derivatives

Compound	λ_{\max} (nm) ^a	log ϵ ^a	p	AQ \times 100
14	443	4.18	16	4.19
15	429	4.14	16	3.70
16	427	3.46	16	0.770
17	429	3.29	16	0.523

^aThe values of λ_{\max} and ϵ were recorded in ethanol.²¹

Conclusions: The vector alignment hypothesis provides a rational approach to the design of intensely colored organic compounds. The hypothesis explains many of the observed variations in the wavelength and intensity of the lowest energy absorbance, between related molecules that differ only by the relative orientations of chromophoric parts (μ -operators). In those cases in which the μ -operators of the constituent parts are collinear, stronger absorption at longer wavelengths is observed, relative to those molecules in which the μ -operators of the parts are oriented either randomly, or parallel but not in line with one another. Thus, the vector alignment hypothesis may assist the rational design of dyes that gather light as effectively as possible for dye-sensitized solar cells, for photodynamic therapy, and other applications.

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