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Article

Excitonic Coupling in Fluorene-Based Bichromophoric Systems: Vibrational Quenching and the Transition from Weak to Intermediate Coupling

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Damian L. Kokkin, Neil J. Reilly, Maxim Ivanov, Rajendra Rathore, and Scott A. Reid*

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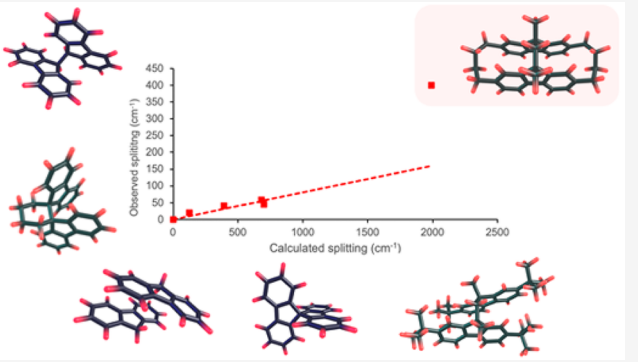
ABSTRACT: Excimeric systems (i.e., excited dimers) have well served as model compounds for the study of the delocalization of electronic energy over weakly interacting chromophores. However, there remain relatively few isolated systems in which such interactions can be studied experimentally at a level to afford detailed comparisons with theory. In this Article, we examine a series of covalently and noncovalently linked dimers of fluorene, as a model aromatic chromophore, where the formation of excimers requires a π-stacked, cofacial orientation at van der Waals contact. Building upon a series of seminal prior studies that examined vibronic quenching of the excitation interaction in van der Waals dimers, the key question that we sought to address here is whether a single quenching factor could reproduce experimental excitonic splittings across a series of covalently and noncovalently linked bichromophoric systems built from the same chromophore. In comparing experimentally measured excitonic splittings with calculated static splittings using time-dependent density functional methods, we find that all systems save one fall on a line with a slope of 0.080(8), reflecting a vibrational quenching of roughly 1 order of magnitude. The outlier, which shows a significantly reduced quenching factor, represents a cyclophane-linked system where the fluorene moieties are constrained in a cofacial arrangement. We argue that this system evidences the transition from the weak to intermediate coupling regime.



INTRODUCTION

Excitonic states involve the delocalization of electronic energy through multiple weakly interacting chromophores. Such interactions are evidenced in a wide variety of important systems and processes, including photosynthesis, molecular crystals and supramolecular assemblies, and of course DNA. As the simplest systems that exhibit excitonic couplings, excimers (or excited dimers) are particularly attractive for study.[1,2] Here the monomeric electronic transition gives rise to two low-lying excited states (S_1/S_2) in the dimer, split by the excitonic interaction. Thus, spectroscopic measurements can be particularly powerful in elucidating the magnitude of this coupling (Davydov splitting).[3] Moreover, such systems can serve as models for understanding excitonic interactions in larger multichromophoric systems.

As highlighted in a recent review,[4] despite decades of study there are relatively few isolated systems where these types of interactions can be studied in sufficient detail to afford detailed comparisons with theory. In a seminal series of papers,[5−14] Leutwyler and co-workers probed excitonic interactions in centrosymmetric hydrogen-bonded dimers built from identical aromatic chromophores, cleverly using isotopic substitution to allow the nominally forbidden $S_0−S_1$ transition to become weakly allowed. They found that static (i.e., Born−Oppenheimer) excitonic splittings, calculated using various ab initio methods, were much larger than the measured splittings by factors of 5−25. This in turn was shown to reflect vibrational quenching due to the Franck−Condon active vibrations of the monomer, which reduces or quenches the purely electronic coupling. As the quenching factor depends on the monomeric Franck−Condon profile, it can be determined from experiment (e.g., by measuring the dispersed fluorescence spectrum from the monomer origin) or from calculations. In showing that the vibrationally quenched splittings reproduced the experimental values well in a number of systems, these

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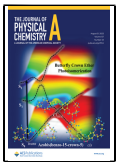

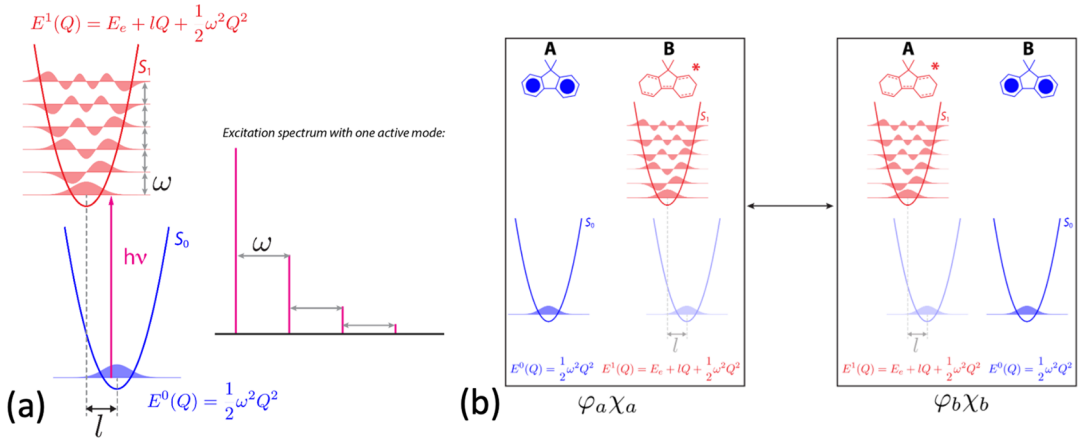

Figure 1. (a) Model chromophore with one active vibrational mode. (b) Diagram illustrating the resonance interaction between two fluorene chromophores. The resulting Hamiltonian can be expressed on an electronic basis with the atomic displacements as parameters.

studies demonstrated that the interaction of vibrational and electronic degrees of freedom is crucial in predicting the properties of excitonic systems. Strong and weak coupling regimes can be delineated by the relative magnitude of the vibronic and electronic couplings, as recognized in early models,[3,15−20] and our understanding of this phenomenon has been refined by more recent theoretical treatments.[6−8,21]

In aromatic systems, the formation of excimers requires a nearly cofacial, π-stacked orientation of chromophores at van der Waals contact, which leads also to charge stabilization.[22] Of the important chromophores, fluorene has been extensively examined as a model π-stacked system,[23−26] with the fluorene dimer extensively studied over the past two decades.[1,2,22,26−33] The Rathore group reported the synthesis and spectroscopic characterization of a novel set of polyfluorenes covalently linked at the 9-position through a single methylene spacer (denoted **Fn**; n = 1−6).[34−37] These molecules adopt a cofacial arrangement in gas, liquid, and solid state and have been utilized as model systems to examine the energy and electron transport in π-stacked assemblies.[38] In a recent communication, we compared experimental excimer stabilization (measured via emission) and charge stabilization (measured via threshold ionization) of covalently linked, cofacially stacked F2 with the van der Waals dimer of fluorene, i.e., $(F)_2$. The measured ionization potentials were identical, yet the excimeric state was stabilized by up to ∼30 kJ/mol in covalently linked F2. Supported by theory, this work demonstrated that optimal stabilization of an excimer requires a perfect sandwich-like geometry with maximal overlap, whereas hole stabilization in π-stacked aggregates is less geometrically restrictive.

In this work, we extend these ideas to examine excitonic splittings in a range of fluorene based dimers, both covalently and noncovalently linked. Building upon the foundational work of Leutwyler and co-workers, a key question that we seek to address here is whether a single quenching factor can reproduce the excitonic splittings across an array of different bichromophoric systems built upon the same chromophore. Importantly, we find that for all systems examined, save one, the experimental excitonic splittings when compared to calculated splittings from time-dependent density functional methods fall on a line with a slope (i.e., quenching factor) of 0.080(8), reflecting a vibrational quenching of roughly 1 order of magnitude. The excluded system, which shows a significantly reduced quenching factor, represents a cyclophane−F2 system, where the aromatic moieties are locked into a cofacial arrangement. We argue that this geometrical restriction, which dramatically alters the quenching factor, provides a view of the transition from the weak to the intermediate coupling regime.

■ ILLUSTRATIVE MODEL OF VIBRATIONAL QUENCHING

Prior to discussing our experimental results, we introduce an illustrative linear vibronic coupling model of vibrational quenching, which may be helpful for the reader. Specifically, as illustrated in Figure 1a, we consider a model fluorene chromophore with a single Franck−Condon active vibrational mode. For the resonance interaction of two fluorene chromophores, Figure 1b, the Hamiltonian can be written on an electronic basis with the atomic displacements as parameters, expressed as[13]

$$\begin{pmatrix} T_n^A + E^1(Q^A) + T_n^B + E^0 + (QB) & V^{AB} \\ V^{AB} & T_n^A + E^0(Q^A) + T_n^B + E^1 + (Q^B) \end{pmatrix} \quad (1)$$

In eq 1, the diagonal terms represent the sum of kinetic (T_n) and potential energy (E^0, E^1) operators for each chromophore (A, B), with the E^0 and E^1 terms further defined in Figure 1, as the rows and columns refer to the locally excited states illustrated in Figure 1b. Here, V^{AB} is the interchromophore electronic coupling. Including a single active mode with a frequency of 500 cm^{-1} and two excitations, we can diagonalize this Hamiltonian and plot the resulting symmetric and antisymmetric states as a function of the coupling parameter V^{AB}. Figure S1 ("S" denotes material in the Supporting Information) provides snapshots of calculated spectra for four different coupling parameters between 50 and 1000 cm^{-1}, which span the regimes of weak to strong coupling. Here red labels the symmetric electronic state and blue labels the asymmetric state. At the highest coupling strength, corresponding to the strong coupling regime, the spectra show two mirrored, well-separated band systems with a splitting of the origins consistent with the purely electronic splitting, given by $2V^{AB}$. For lower coupling strengths, there is significant vibronic mixing, which can give rise to more complicated patterns. Here, the splitting of origins is much smaller than the purely electronic splitting, reflecting the phenomenon of vibrational quenching described above.

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EXPERIMENTAL AND THEORETICAL METHODS

Resonant 2-photon ionization (R2PI) studies of jet-cooled samples were carried out in a 1 m linear time-of-flight (TOF) mass spectrometer, which has previously been described in detail.[39] Resonant excitation and ionization were achieved using the frequency doubled output of a Nd:YAG pumped dye laser (Lambda-Physik Scanmate 2E pumped by the third harmonic of a Quantel Q-Smart 850 Nd:YAG laser). In two-color experiments, denoted as 2CR2PI, a second photon was used for ionization, which came either from the 266 nm output of a second Nd:YAG system (Continuum Minilite) or the tunable frequency doubled output of a second Nd:YAG pumped dye laser (Sirah Cobra-Stretch pumped by the second harmonic of a Spectra-Physics INDI Nd:YAG laser). Excitation and ionization lasers were overlapped spatially and temporally and counterpropagated through the TOF spectrometer. Temporal control of the experiment was achieved by use of an 8-channel digital pulse/delay generator (Berkeley Nucleonics 565).

Fluorescence excitation and emission spectra were measured in a separate apparatus, which has previously been described in detail.[40−42] The fluorescence measurements employed a mutually orthogonal geometry for laser, molecular beam, and detector, where the laser beam crossed the molecular beam at a distance of ∼15 mm downstream. The resulting fluorescence was imaged by a two-lens system through a long-pass cutoff filter onto a photomultiplier tube detector (PMT, Oriel 77348). Dispersed fluorescence spectra were obtained by imaging the fluorescence onto the slit of a 0.55 m monochromator/spectrograph (Horiba iHR550) equipped with a PMT detector (Oriel 77348). Spectra were acquired by integrating the PMT output using a gated integrator (Stanford Research SR250), with the output signal digitized by a 12-bit ADC (Measurement Computing USB-1208FS) prior to further processing. A LABVIEW coded program was developed for data collection, laser wavelength, and monochromator control.

To support our experimental findings, electronic structure calculations were performed using the GAUSSIAN 09 software package.[43] Benchmarking studies of the benzene dimer showed that accurate ground and excited state energies could be obtained using a PBE0 density functional[44−46] augmented with the D3 version of Grimme's dispersion term.[47] Thus, we performed geometry optimizations and subsequent time-dependent density functional calculations using the PBE0-D3 method with an aug-cc-pVDZ basis set.[48,49]

RESULTS AND DISCUSSION

Figure S2 shows the structures of all of the fluorene-based bichromophoric compounds examined in this work. Below we discuss the spectroscopic analysis of each in turn, focusing on the experimental measurement and theoretical prediction of the S_1/S_2 splitting.

Spirobifluorene. The spectrum of spirobifluorene has been previously measured under jet-cooled conditions by Levy and co-workers.[50,51] Our jet-cooled spectrum, as measured using two-color R2PI (2CR2PI) spectroscopy, is shown in Figure S3 in the Supporting Information (SI). Given the perpendicular orientation of the two chromophores, the coupling in this case vanishes, and the S_1/S_2 states are degenerate.

Fluorene Dimer (van der Waals). The spectrum of the van der Waals dimer of fluorene was first measured by Itoh and co-workers,[27] and later by Lim and co-workers[30,52] and Wessel et al. using laser-induced fluorescence (LIF) spectroscopy.[53] Despite these extensive studies, the spectrum has defied a detailed analysis. The origin region evidences two short progressions, with the members broadened homogeneously, indicative of a few ps lifetime. We have recently remeasured this spectrum using R2PI spectroscopy and conducted hole-burning measurements that confirm that the features derive from a single species.[54] Our interpretation is that the homogeneous broadening arises from a rapid rearrangement in the excited state to a stacked excimeric structure, from which emission occurs. The band origins of the two intermolecular progressions, which differ in frequency, are assigned to the electronic origins of the S_1 and S_2 states, split by 20 cm^{-1}, as illustrated in Figure S4 in the SI. Reflecting the phenomenon of vibrational quenching described above, this splitting is much smaller than the TD-PBE0-D3/aug-cc-pVDZ prediction of 127 cm^{-1} (Table 1).

Table 1. Calculated and Observed S_1/S_2 (Excitonic) Splittings

species	calcd splitting in cm^{-1}	obs splitting in cm^{-1}	predicted splitting from fit
spirobifluorene	0.0	0.0	0.0
fluorene vdW dimer	127	20	10
1,2-bifluorenylcyclohexane	391	41	31
9,9′-bifluorene	679	58	55
t-butyl F2	701	46	56
cyclophane F2	1988	386	160

9,9′-Bifluorene. The spectrum of 9,9′-bifluorene has been previously measured under jet-cooled conditions by Levy and co-workers.[50] Our spectrum, measured using LIF spectroscopy, is shown in Figure S5 in the SI. The splitting of the S_1 and S_2 origins here is 58 cm^{-1}, which may be compared with the TD-PBE0-D3/aug-cc-pVDZ prediction of 679 cm^{-1} (Table 1).

1,2-Bifluorenylcyclohexane. The synthesis and characterization of 1,2-bifluorenylcyclohexane are detailed in Scheme S1 in the SI. Figure 2 shows the low energy region of the R2PI spectrum of 1,2-bifluorenylcyclohexane measured under jet-cooled conditions. Two band systems are clearly observed, and the major vibrational progressions in each is marked. As shown in Figures S6 and S7 of the SI, these progressions could be well fit by a simple harmonic progression up to at least five quanta. The fit of the S_1 data returned a vibrational frequency of 33 cm^{-1}, consistent with a low frequency torsional mode that involves "butterfly"-like motion of the two fluorenes. The splitting of the S_1 and S_2 origins derived from these fits is 41 cm^{-1}, which may be compared with the TD-PBE0-D3/aug-cc-pVDZ prediction of 391 cm^{-1} for the S_1/S_2 splitting (Table 1).

***tert*-Butyl F2.** As noted above, we previously reported the spectra of a model covalently linked fluorene dimer, F2.[54] Unfortunately, due to spectral congestion imparted by torsional dynamics, it was not possible to obtain information about the S_1/S_2 splitting in the model system. We therefore examined substituted analogues that were more hindered, including a ditertbutyl derivative (*t*-butyl-F2). Figure 3 shows the LIF spectra of this compound near its electronic origin. This spectrum was reported in preliminary work,[55] but was not

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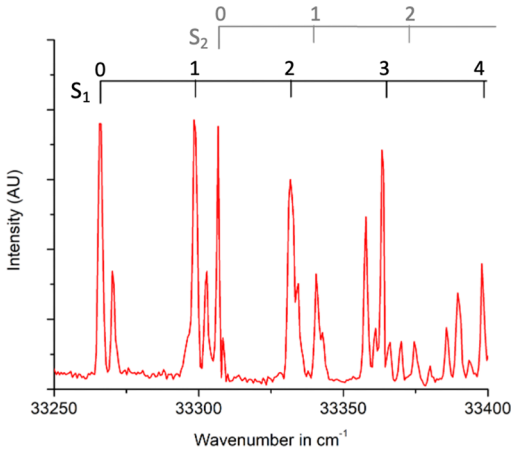

Figure 2. Resonant 2-photon ionization (R2PI) spectrum of 1,2-bifluorenylcyclohexane in the region of the electronic origin. The major progressions in the two observed band systems are identified, fits of these are provided in the Supporting Information.

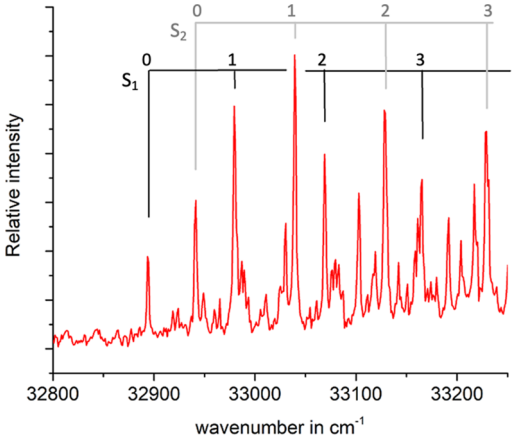

Figure 3. LIF spectrum of the *t*-butyl−F2 molecule in the region of the electronic origin. The major progressions in the two observed band systems are identified, fits of these are provided in the Supporting Information.

analyzed in detail. Two band systems are clearly observed, and the major vibrational progression in each is identified. As shown in Figures S8 and S9 of the ESI, these progressions could be well fit by a simple harmonic progression of up to at least five quanta. The fit for S_1 returned a vibrational frequency of ∼45 cm^{-1}, consistent with a low frequency torsional mode which again corresponds to a "butterfly" like motion of the two fluorene rings, reflecting the drive toward cofaciality in the excited state. The associated frequency for the S_2 state is higher, roughly 62 cm^{-1} (Figure S9). The splitting of the S_1 and S_2 origins derived from these fits is 46 cm^{-1}, which can be compared with the TD-PBE0-D3/aug-cc-pVDZ prediction of 701 cm^{-1} for the S_1/S_2 splitting (Table 1).

Cyclophane F2. Finally, we examined a cyclophane F2 system where the aromatic moieties were locked into a cofacial arrangement. Figure 4 shows the LIF spectra of this compound near its electronic origin. This spectrum was also reported in preliminary work,[55] but was not analyzed in detail. Two well-separated band systems are clearly observed, and the major vibrational progression in each is identified. Here, the Franck−Condon activity is still dominated by the "butterfly" like torsion; however, this mode has shifted upward in frequency to

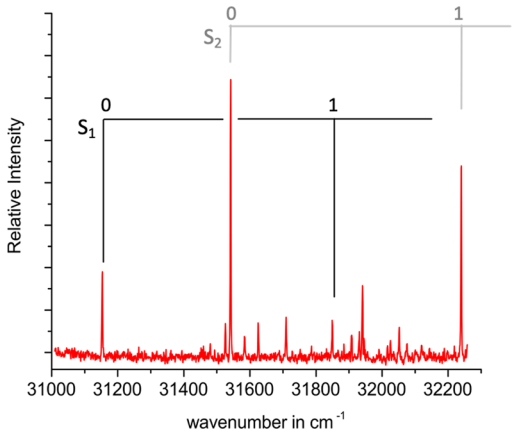

Figure 4. LIF spectrum of the cyclophane−F2 molecule in the region of the electronic origin. The major progressions in the two observed band systems are identified.

700 cm^{-1}. Consistent with this observation, the single vibronic level (SVL) emission spectrum measured from the S_2 origin shows a single progression with a ground state vibrational frequency of 750 cm^{-1} (Figure S10). The splitting of the S_1 and S_2 origins derived from the spectra is 386 cm^{-1}, which can be compared with the TD-PBE0-D3/aug-cc-pVDZ prediction of 1988 cm^{-1} for S_1/S_2 splitting (Table 1). We also note that the relative intensity of the two origin transitions is ∼3.3, which may be compared with the ratio of 6.5 predicted at the TD-PBE0-D3/aug-cc-pVDZ level.

Figure 5 displays a graphical comparison of the observed and calculated S_1/S_2 splittings for the fluorene based bichromophoric systems considered here. With the exception of the cyclophane F2 system, the data for other systems fall roughly (R^2 = 0.96) on a straight line passing through the origin, with a slope of 0.080(8), where the uncertainty represents one standard error. This represents a vibrational quenching of the excitonic interaction of roughly 1 order of magnitude. In the weak coupling regime, the vibrational quenching may be estimated by performing a Franck−Condon analysis of the monomer, in this case fluorene. The quenching factor can be determined theoretically from calculation of the relevant Franck−Condon factors, or experimentally via measurement of the S_0−S_1 spectrum. As described by Leutwyler,[14] an estimate of the quenching factor (Γ) may be derived from the following expression:

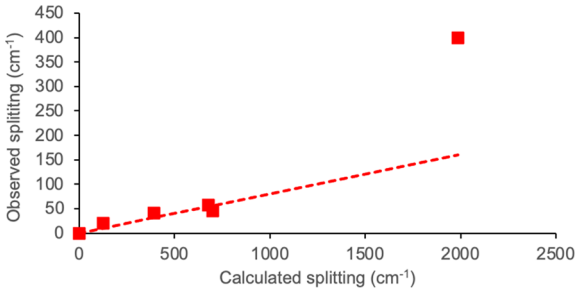

Figure 5. Plot of observed S_1/S_2 splittings in the bifluorene molecules investigated in this work, vs those calculated at the TD-PBEO-D3/aug-cc-pVDZ level. A linear fit to the data for all systems apart from the cyclophane−F2 system is shown.

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$$\Gamma = \exp\left(-\sum_i S_i\right) \tag{2}$$

where the sum extends over all optically active modes (i) and the factor S_i is given by

$$S_i = \frac{\mathrm{FCF}(i_0^1)}{\mathrm{FCF}(O_0^0)} \tag{3}$$

In eq 3 the numerator and denominator represent the Franck–Condon factors for the optically active mode i and the origin, respectively. To avoid issues with saturation and nonradiative excited state processes which may influence the experimental excitation spectra, we chose to determine the S_i values experimentally from the dispersed emission spectrum obtained following excitation of the vibrationless level of fluorene. The resulting quenching factor obtained was $\Gamma = 0.089$, which is in very reasonable agreement with that determined experimentally from the slope of the fit line in Figure 5. As a further check, we also estimated Γ from the calculated excitation spectrum obtained at the TD-PBEO-D3/aug-cc-pVDZ level of theory. This returned a slightly higher value for Γ of 0.12, still in reasonable agreement with experiment.

The cyclophane–F2 system is the lone system found to deviate from this linear relationship. Due to the enforced cofaciality imposed by the cyclophane linkages, the electronic coupling in this case is dramatically increased, with the calculated excitonic splitting more than 3 times that of the sterically hindered but noncofacial *t*-butyl–F2 (Table 1), and the quenching factor is also increased. We argue that this system illustrates the transition from the weak coupling regime, where most systems will reside, to an intermediate coupling regime.

CONCLUSIONS

We report here a study of the effects of vibrational quenching of electronic excitonic splittings in a series of fluorene-based bichromophores that are either covalently or noncovalently linked. The key issue addressed by this study is whether, in the weak coupling regime, a single quenching factor can reproduce splittings across a range of systems built upon the same chromophore. We find that for the systems studied here, except one, the experimentally derived excitonic splittings when plotted against the theoretically predicted static splittings fall roughly on a straight line with slope of 0.080(8), which indicates a vibrational quenching of roughly 1 order of magnitude. The lone outlier is a cyclophane-based system where the fluorene moieties are "locked" into a cofacial conformation. Here the electronic coupling is significantly increased and quenching is significantly reduced, which we argue reflects the transition from the weak to intermediate regimes of vibronic coupling.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.3c03511.

Ten additional figures and one scheme that include structures for each of the molecules examined in this work and additional spectroscopic data and analysis (PDF)

AUTHOR INFORMATION

Corresponding Author

Scott A. Reid − *Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233, United States;* orcid.org/0000-0001-9916-7414; Phone: (414) 288-7565; Email: scott.reid@marquette.edu

Authors

Damian L. Kokkin − *Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233, United States*

Neil J. Reilly − *Department of Chemistry, University of Massachusetts-Boston, Boston, Massachusetts 02125, United States;* orcid.org/0000-0001-5572-4784

Maxim Ivanov − *Amgen Inc., Thousand Oaks, California 91320, United States*

[‖]**Rajendra Rathore** − *Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233, United States; Department of Chemistry, University of Massachusetts-Boston, Boston, Massachusetts 02125, United States; Amgen Inc., Thousand Oaks, California 91320, United States;* orcid.org/0000-0001-7387-7936

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpca.3c03511

Notes

The authors declare no competing financial interest.

[‖]Deceased February 16, 2018.

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