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First Experimental Evidence for the Diverse Requirements of Excimer vs Hole Stabilization in π-Stacked Assemblies

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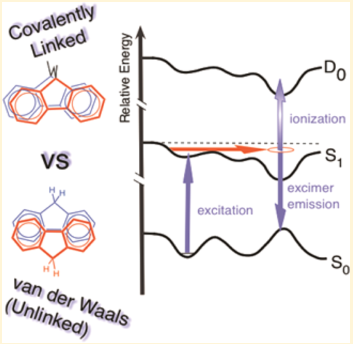
Supporting Information

ABSTRACT: Exciton formation and charge separation and transport are key dynamical events in a variety of functional polymeric materials and biological systems, including DNA. Beyond the necessary cofacial approach of a pair of aromatic molecules at van der Waals contact, the extent of overlap and necessary geometrical reorganization for optimal stabilization of an excimer vs dimer cation radical remain unresolved. Here, we compare experimentally the dynamics of excimer formation (via emission) and charge stabilization (via threshold ionization) of a novel covalently linked, cofacially stacked fluorene dimer (F2) with the unlinked van der Waals dimer of fluorene, that is, $(F)_2$. Although the measured ionization potentials are identical, the excimeric state is stabilized by up to ~30 kJ/mol in covalently linked F2. Supported by theory, this work demonstrates for the first time experimentally 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.



The dynamics of exciton and hole formation and migration in π-stacked assemblies are central to the mechanisms of biological systems and the development of functional polymeric materials.[1] As the simplest units capable of excimer formation and charge delocalization, dimers of benzene,[2,3] fluorene,[4,5] naphthalene,[6] and pyrene[7] have served as models for understanding excitonic interactions and electron transfer in multichromophoric assemblies.[8−10] Though it is appreciated that π-stacked assemblies stabilize both charge and excitation energy, the geometrical reorganizations and underlying mechanisms accompanying these important events are not well understood nor, indeed, is there a unified understanding of π-stacking interactions.[11,12]

Representing a significant advance in our ability to study π-stacked aggregates, 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**; $n = 1{-}6$).[13−17] These molecules adopt a cofacial arrangement in gas, liquid, and solid state and have been utilized as model systems to examine energy and electron transport in π-stacked assemblies.[18] Herein, we use F2 as a model covalently linked system, which we compare with the unlinked (i.e., van der Waals) dimer of fluorene, that is, $(F)_2$ in order to examine the geometrical requirements for excimer vs dimer cation radical stabilization. Utilizing a powerful experimental approach in vacuo which monitors emission or delayed ionization from the excimeric states, we compare emission and resonant ionization spectra of the two dimers, which affords a facile comparison of the relative stabilization of excimer vs hole (i.e., cation radical). We thus probe for the first time the relative efficiency and geometrical requirements of excimer formation vs charge stabilization in a model bichromophore.

A schematic of the experiment is shown in Figure 1. Our studies were carried out on isolated cold (T_{rot} ~ 20 K) molecules in the gas-phase using a supersonic nozzle; details are provided in the Supporting Information (SI). In each case, laser excitation from the ground state minimum placed the dimer on the S_1 surface, where rapid rearrangement resulted in excimer

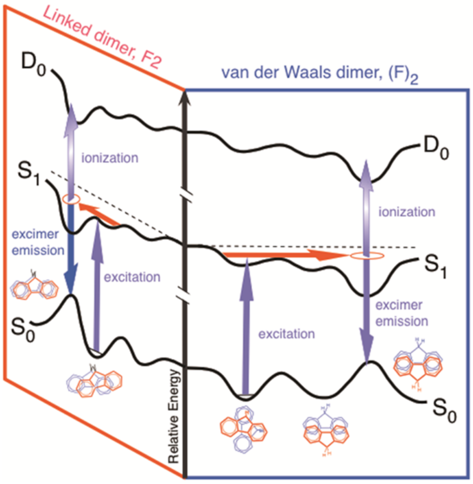


Figure 1. Experimental schematic. For both covalently linked F2 and the van der Waals dimer $(F)_2$, excitation of the isolated dimer leads to rapid excimer formation, which is probed by monitoring emission, or by delayed ionization.

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formation, evidenced in the dominance of excimer emission and a lengthened fluorescence lifetime. Analysis of line widths in the $(F)_2$ spectrum (Figure S1) indicate a time scale for this process of several picoseconds, consistent with recent studies of the benzene dimer.[19] From the excimeric well, absorption of a photon from a second laser pulse, delayed by ∼5 ns, led to ionization; scanning the energy of the second photon while monitoring the mass signature of interest generated an ion yield curve, from which the ionization threshold was extracted.

Gas-phase emission spectra of F2 and $(F)_2$ are compared in Figure 2 with the solution phase spectrum of F2, measured in dichloromethane. All spectra show a broad, red-shifted feature characteristic of excimeric emission, and the lifetime of the F2 emission, of order 60 ns, is similar to the reported lifetime (54 ns) of $(F)_2$.[6] However, the position of the F2 emission feature is shifted to longer wavelength by some 40 nm from that of $(F)_2$, indicating significant (up to ∼30 kJ/mol) stabilization of the excimer in the covalently linked system. We suggest that this stabilization arises from the ability of the covalently linked dimer to form a perfect sandwich structure, which is not possible in the van der Waals dimer due to steric repulsion. Interestingly, the solution and gas-phase spectra of F2 are similar, revealing little solvochromatic effect.

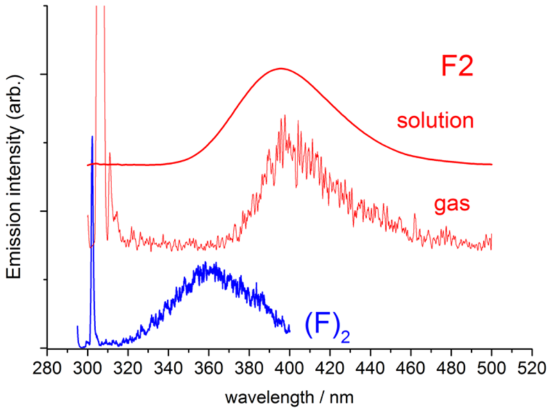

Figure 2. Emission spectra of F2 and $(F)_2$ in the gas phase. Also shown for comparison is the solution phase spectrum of F2.

To probe the degree of stabilization of the cation radicals in the two dimers, ionization thresholds were determined using two-color ionization. Photoionization from the excimer well is expected to show favorable Franck−Condon factors, owing to the similar geometries of excimer and cation radical. However, under our conditions no collisional relaxation occurs on the time scale of the experiment, and ionization therefore occurs from highly excited vibrational levels in the excimer well, giving rise to a gradual onset in the dimer ion yield curves, shown in Figure 3, which compares ion yield curves for F2 and $(F)_2$ (upper panel) with that of the fluorene monomer. The dimers display identical ionization thresholds of ∼7.51(1) eV, significantly lowered by ∼0.38 eV or 40 kJ/mol relative to the monomer (7.885(5) eV). Thus, the cation radical state is stabilized in the dimers, as expected, but surprisingly to a *similar* degree. This strongly suggests that, in comparison with excimer formation, stabilization of the cation radical does not require optimum overlap; that is, that the geometrical requirements for hole stabilization are less restrictive.[20] Note that the IP of F2 determined here via two-color ionization is consistent with an prior determination from photoelectron spectroscopy.[13]

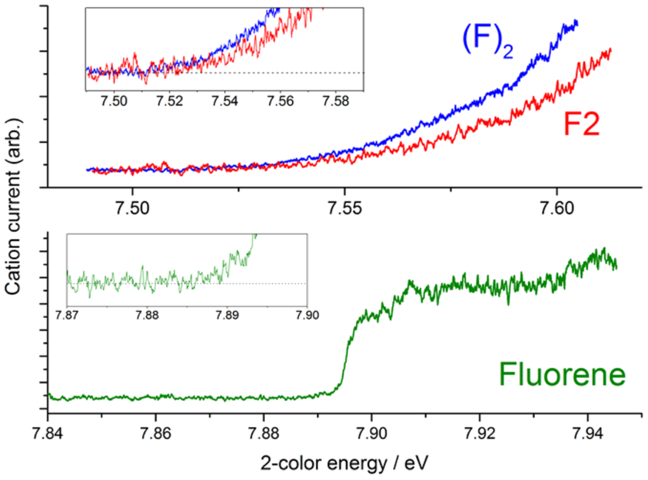

Figure 3. Ion yield curves of $(F)_2$, F2 and fluorene monomer.

Our experimental findings are consistent with computational studies of the relevant potential energy surfaces. Due to the importance of electron correlation in the proper description of π-stacking interactions, we performed a brief benchmarking study of the benzene dimer;[21] details are provided in the SI. We found that accurate energies could be obtained using a simple PBE0 density functional[22,23] augmented with the D3 version of Grimme's dispersion term,[24] at a fraction of the cost of more sophisticated methods (Table S1). Thus, ground state calculations were performed at the PBE0-D3 level with a def2-TZVP basis set.[25,26] Excited electronic states were computed with time-dependent DFT at the PBE0-D3 level with def2-TZVP or def2-SV(P) basis sets. For the cation radical states, a calibrated[27−29] B1LYP functional (B1LYP-40) was employed, with a 6-31G(d) basis set; wave function stability tests were performed to ensure the absence of states with lower energy.

Figure 4 displays the energies of relevant points on the singlet PESs of $(F)_2$, at left, and F2. The global minimum of the van der Waals dimer corresponds to a parallel orthogonal conformer, which is consistent with the experimental finding of

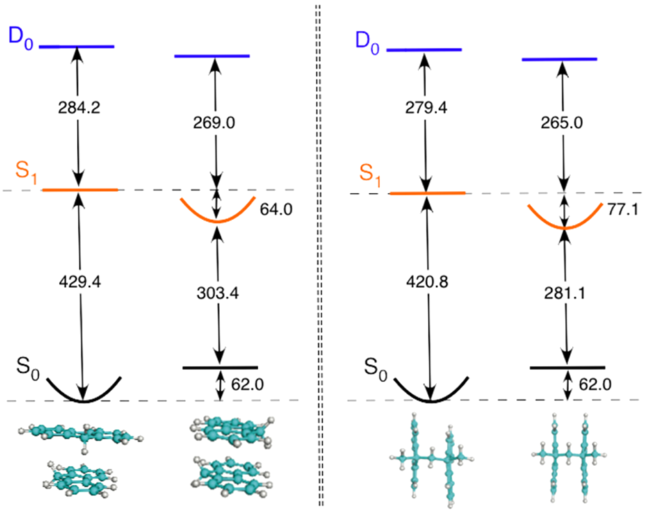

Figure 4. Calculated points on the potential energy surfaces of $(F)_2$ (at left) and F2. Parabolas indicate where geometry optimizations were performed.

excitonic bands bearing nearly equal intensity (Table S2).[5] On the S_1 surface, the head-to-tail sandwich excimer structure is the global minimum, lying ~64 kJ/mol below the vertical energy of the locally excited (LE) state. Vertical ionization requires 333 kJ/mol of energy from the bottom of the excimer well.

For the covalently linked F2, the ground state minimum is a cofacial parallel−displaced structure, and the excimer lies ~77 kJ/mol below the vertical energy of the LE state. The increased stabilization of the F2 excimer, by some 25%, as predicted by theory is roughly consistent with the observed experimental red-shift of the excimeric emission relative to $(F)_2$, Figure 2. Vertical ionization of F2 requires 342 kJ/mol of energy from the bottom of the excimer well. Thus, our calculations support the experimental finding that the excimeric state is stabilized in the covalently linked dimer, whereas the vertical ionization energies of the two dimers are predicted to be similar.

Additional insights are provided from study of the van der Waals dimer of F1; that is, the 9,9′-dimethyl derivative, details of which will be reported in a future publication. As shown in Figure 2 in the SI, gas-phase emission spectra of $(F1)_2$ show beautifully resolved torsional structure which affords ready assignment to the head-to-tail π-stacked dimer. *Surprisingly, there is no evidence of excimeric emission*! This is rationalized as due to the increased steric constraints imposed by the methyl substituents, which prevents a sandwich overlap of the chromophores. In contrast, the measured IP of $(F1)_2$ is 7.58(1) eV, which lies above that of F2 and $(F)_2$ but still evidence significant stabilization relative to the monomer.

These findings highlight the diverse geometrical requirements inherent to excimer formation vs cation radical stabilization in a π-stacked bichromophore, which we have explored by exploiting the fact that processes of ionization and emission occur from the (same) excimeric state in the isolated molecules. Excimer formation, which is dominated by exciton resonance and π-stacking, is favored by a perfect “sandwich” overlap of the two chromophores.[30] This is maximal in the covalently linked dimer, whereas steric constraints lead the van der Waals dimer to stack in a head-to-tail arrangement (Figure 4). The geometrical requirements for cation radical stabilization, which involves significant charge transfer, are less restrictive.

In organic-based electronic devices, excimer formation serves to trap generated excitons, hindering charge separation. Understanding the geometrical requirements for excimer formation vs hole stabilization thus provides valuable insights for the design of new multichromophoric assemblies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b01201.

> Materials and methods; potential energy surface profiles for $(F)_2$, F2 and F2H2; S_1/S_2 states and V_{ab} coupling; additional references. (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Hoeben, F. J.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. About Supramolecular Assemblies of Π-Conjugated Systems. *Chem. Rev.* **2005**, *105*, 1491−1546.

(2) Hirata, T.; Ikeda, H.; Saigusa, H. Dynamics of Excimer Formation and Relaxation in the T-Shaped Benzene Dimer. *J. Phys. Chem. A* **1999**, *103*, 1014−1024.

(3) Balmer, F. A.; Trachsel, M. A.; van der Avoird, A.; Leutwyler, S. The Elusive S2 State, the S1/S2 Splitting, and the Excimer States of the Benzene Dimer. *J. Chem. Phys.* **2015**, *142*, 234306.

(4) Saigusa, H.; Lim, E. C. Localized and Delocalized Excited States of the Fluorene Dimers. *J. Phys. Chem.* **1991**, *95*, 1194−1200.

(5) Wessel, J.; Beck, S.; Highstrete, C. Excitonic Interaction in the Fluorene Dimer. *J. Chem. Phys.* **1994**, *101*, 10292−10302.

(6) Saigusa, H.; Lim, E. C. Excimer Formation in Van Der Waals Dimers and Clusters of Aromatic Molecules. *Acc. Chem. Res.* **1996**, *29*, 171−178.

(7) Duhamel, J. New Insights in the Study of Pyrene Excimer Fluorescence to Characterize Macromolecules and Their Supramolecular Assemblies in Solution. *Langmuir* **2012**, *28*, 6527−6538.

(8) Chipot, C.; Jaffe, R.; Maigret, B.; Pearlman, D. A.; Kollman, P. A. Benzene Dimer: A Good Model for Π-Π Interactions in Proteins? A Comparison between the Benzene and the Toluene Dimers in the Gas Phase and in an Aqueous Solution. *J. Am. Chem. Soc.* **1996**, *118*, 11217−11224.

(9) Amicangelo, J. C. Theoretical Study of the Benzene Excimer Using Time-Dependent Density Functional Theory. *J. Phys. Chem. A* **2005**, *109*, 9174−9182.

(10) Sinnokrot, M. O.; Sherrill, C. D. High-Accuracy Quantum Mechanical Studies of Pi-Pi Interactions in Benzene Dimers. *J. Phys. Chem. A* **2006**, *110*, 10656−10668.

(11) Hunter, C. A.; Sanders, J. K. The Nature of Pi-Pi Interactions. *J. Am. Chem. Soc.* **1990**, *112*, 5525−5534.

(12) Martinez, C. R.; Iverson, B. L. Rethinking the Term Pi-Stacking. *Chemical Science* **2012**, 3, 2191−2201.

(13) Rathore, R.; Abdelwahed, S. H.; Guzei, I. A. Synthesis, Structure, and Evaluation of the Effect of Multiple Stacking on the Electron-Donor Properties of Pi-Stacked Polyfluorenes. *J. Am. Chem. Soc.* **2003**, *125*, 8712−8713.

(14) Rathore, R.; Chebny, V. J.; Abdelwahed, S. H. A Versatile and Conformationally Adaptable Fluorene-Based Receptor for Efficient Binding of Silver Cation. *J. Am. Chem. Soc.* **2005**, *127*, 8012−8013.

(15) Rathore, R.; Abdelwahed, S. H.; Kiesewetter, M. K.; Reiter, R. C.; Stevenson, C. D. Intramolecular Electron Transfer in Cofacially Pi-Stacked Fluorenes: Evidence of Tunneling. *J. Phys. Chem. B* **2006**, *110*, 1536−1540.

(16) Chebny, V. J.; Rathore, R. Convergent Synthesis of Alternating Fluorene-P-Xylene Oligomers and Delineation of the (Silver) Cation-Induced Folding. *J. Am. Chem. Soc.* **2007**, *129*, 8458−8465.

(17) Nakano, T. Synthesis, Structure and Function of Π-Stacked Polymers. *Polym. J.* **2010**, *42*, 103−123.

(18) Vura-Weis, J.; Abdelwahed, S. H.; Shukla, R.; Rathore, R.; Ratner, M. A.; Wasielewski, M. R. Crossover from Single-Step

Tunneling to Multistep Hopping for Molecular Triplet Energy Transfer. *Science* **2010**, *328*, 1547−1550.

(19) Miyazaki, M.; Fujii, M. Real Time Observation of the Excimer Formation Dynamics of a Gas Phase Benzene Dimer by Picosecond Pump-Probe Spectroscopy. *Phys. Chem. Chem. Phys.* **2015**, *17*, 25989−25997.

(20) Navale, T. S.; Thakur, K.; Vyas, V. S.; Wadumethrige, S. H.; Shukla, R.; Lindeman, S. V.; Rathore, R. Charge Delocalization in Self-Assembled Mixed-Valence Aromatic Cation Radicals. *Langmuir* **2012**, *28*, 71−83.

(21) Sinnokrot, M. O.; Sherrill, C. D. Highly Accurate Coupled Cluster Potential Energy Curves for the Benzene Dimer: Sandwich, T-Shaped, and Parallel-Displaced Configurations. *J. Phys. Chem. A* **2004**, *108*, 10200−10207.

(22) Perdew, J. P.; Ernzerhof, M.; Burke, K. Rationale for Mixing Exact Exchange with Density Functional Approximations. *J. Chem. Phys.* **1996**, *105*, 9982−9985.

(23) Adamo, C.; Barone, V. Accurate Excitation Energies from Time-Dependent Density Functional Theory: Assessing the PBEO Model for Organic Free Radicals. *Chem. Phys. Lett.* **1999**, *314*, 152−157.

(24) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (Dft-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.

(25) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297−3305.

(26) Weigend, F. Accurate Coulomb-Fitting Basis Sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057−1065.

(27) Renz, M.; Theilacker, K.; Lambert, C.; Kaupp, M. A Reliable Quantum-Chemical Protocol for the Characterization of Organic Mixed-Valence Compounds. *J. Am. Chem. Soc.* **2009**, *131*, 16292−16302.

(28) Renz, M.; Kess, M.; Diedenhofen, M.; Klamt, A.; Kaupp, M. Reliable Quantum Chemical Prediction of the Localized/Delocalized Character of Organic Mixed-Valence Radical Anions. From Continuum Solvent Models to Direct-Cosmo-Rs. *J. Chem. Theory Comput.* **2012**, *8*, 4189−4203.

(29) Talipov, M. R.; Boddeda, A.; Timerghazin, Q. K.; Rathore, R. Key Role of End-Capping Groups in Optoelectronic Properties of Poly-P-Phenylene Cation Radicals. *J. Phys. Chem. C* **2014**, *118*, 21400−21408.

(30) Talipov, M. R.; Ivanov, M. V.; Reid, S. A.; Rathore, R. Two's Company, Three's a Crowd: Exciton Localization in Cofacially Arrayed Polyfluorenes. *J. Phys. Chem. Lett.* **2016**, 2915−2920.