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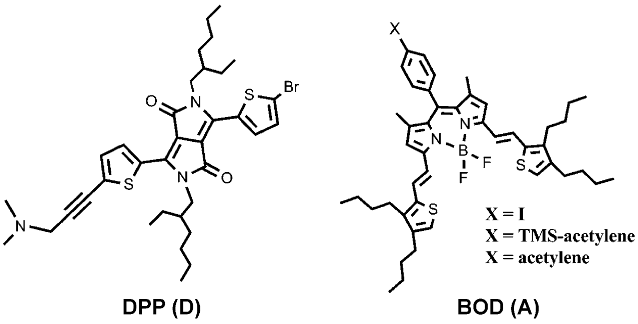
VIP Photophysics

Through-Space Electronic Energy Transfer Across Proximal Molecular Dyads**

Anthony Harriman, Mohammed A. H. Alamiry, Jerry P. Hagon, Delphine Hablot, and Raymond Ziessel**

The rate constant (k_{EET}) for electronic energy transfer between well-defined chromophores can be employed as a means to determine structural information about the system under investigation.[1] The most notable examples arise from biochemistry where protein-bound reactants are separated by 30 Å or more and where there are only very weak electronic interactions.[2] Under such conditions, the Förster coulombic mechanism[3] is likely to hold and multipole interactions can be ignored. In certain cases, the separation distance and/or mutual orientation of the reactant pair can be deduced from spectroscopic observations. It is often considered[4] that this ideal dipole approximation will breakdown at shorter separations but hard experimental evidence for such behavior is scarce. In fact, it has been shown[5] that Förster theory gives an acceptable account of experimental k_{EET} values at 20 Å separations, at least in certain situations, while even smaller separations become possible[6] when the reactants possess unusually short transition dipole moment vectors. It has also been shown[7] that supposedly rigid organic frameworks are subject to considerable out-of-plane bending in fluid solution at ambient temperature. Such structural fluctuations might contribute significantly to the observed k_{EET} values if the lowest-energy conformation imposes orthogonality on the respective transition dipole moment vectors.[8] Alternative protocols for expressing electronic energy transfer (EET) between closely spaced but weakly coupled reactants are available but have not been well-tested with molecular dyads. Such treatments include the extended dipole approach, introduced by Kuhn and co-workers,[9] where the point dipoles inherent to Förster theory are replaced with a linear dipole of fixed length. More rigorous treatments include the atomistic approach,[10] where the transition dipole moments are broken down into contributions for each atom, and the transition density cube[11] that does a similar job over the entire wave function.

Herein, we compare experimental and computed k_{EET} values for three carefully selected molecular dyads that differ in terms of the geometry of the central connector. In each case, the donor (D) is a diketopyrrolopyrrole (DPP) dye[12] while the corresponding acceptor (A) is an extended boron dipyrromethene (Bodipy) dye fitted with ethenylthiophene units as the conjugation extenders (Scheme 1);[13] see the Supporting Information for synthesis of D[14] and A. The critical part of these molecular dyads relates to the bridges that serve to impose structural integrity while minimizing electronic connectivity between the terminals. Two of these bridges are formed by carborane clusters[15] that provide either *para* or *ortho* linkages while the shortest dyad has a phenylethynylenethienyl connector (Scheme 2).



Scheme 1. Molecular formulae of the donor and acceptor modules.

The target dyads were synthesized step-by-step from the pre-organized *para*- and *ortho*-carborane and modules D and A. For the synthesis of DPP-Cp-BOD, two orthogonal functions (a terminal alkyne and a triethylsilyl alkyne) were built onto the bridge.[16] Three steps are needed to reach the target: 1) cross-coupling BOD(alkyne) with C_p, 2) removal of the TES group, and 3) cross-coupling with DPP. Four steps are needed to prepare DPP-Co-BOD: 1) statistical reaction with BOD(alkyne), 2) grafting of trimethylsilylacetylene, 3) deprotection, and 4) cross-coupling with D. The directly linked dyad was prepared from DPP and BOD(alkyne) using a Pd catalyst. All compounds are reasonably soluble in organic solvents, without sign of aggregation, and stable over prolonged storage in the dark.

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[*] Prof. Dr. A. Harriman, Dr. M. A. H. Alamiry, Dr. J. P. Hagon
Molecular Photonics Laboratory, School of Chemistry
Bedson Building, Newcastle University
Newcastle upon Tyne, NE1 7RU (UK)
E-mail: anthony.harriman@ncl.ac.uk
Homepage: http://ncl.ac.uk/mpl
D. Hablot, Dr. R. Ziessel
Laboratoire de Chimie Organique et Spectroscopie Avancées
ICEEPS-LCOSA
25 Rue Becquerel, 67087 Strasbourg Cedex (France)
E-mail: ziessel@unistra.fr
Homepage: http://icpees.unistra.fr/chimie-fonctionnelle-spectroscopie-et-reactivite/chimie-organique-et-spectroscopies-avancees/

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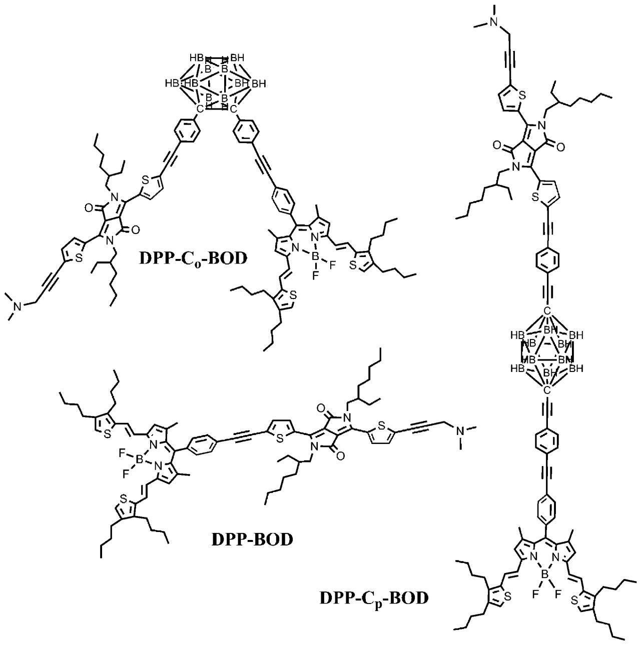

Scheme 2. Molecular formulae for the three molecular dyads described herein. DPP-C_O-BOD and DPP-C_P-BOD are bridged by carborane clusters. See the Supporting Information for the energy-minimized structures.

The molecular conformation computed for the *para* derivative, DPP-C_P-BOD, indicates a linear geometry with the centers of the terminal chromophores being separated by 35.8 Å (see Figure S1 in the Supporting Information). The absorption spectrum recorded in 2-methyltetrahydrofuran (MTHF) shows contributions from both DPP ($\lambda_{max} = 605$ nm, $\varepsilon_{max} = 43{,}000\,\text{M}^{-1}\text{cm}^{-1}$) and Bodipy ($\lambda_{max} = 672$ nm, $\varepsilon_{max} = 130\,000\,\text{M}^{-1}\text{cm}^{-1}$) units (Figure 1). Fluorescence is readily observed from both dyes ($\lambda_{FLU} = 627$ nm for DPP and 687 nm for Bodipy) under conditions where DPP is the predominant (i.e., >90%) absorber (Figure 1). Excitation spectra (Figure S2) confirm that intramolecular EET occurs from DPP to Bodipy under these conditions and comparison with control compounds[17] indicates that the probability of EET exceeds 90%. This high efficacy for EET is to be expected because of the excellent spectral overlap (see Figure S3). Time-resolved emission spectroscopy made with time-correlated, single-photon counting methodology indicates a lifetime (τ_S) for the fluorescent state of DPP of 290 ± 15 ps. This can be compared with a value of 5.2 ± 0.1 ns for the isolated donor. Furthermore, fluorescence characteristic of the acceptor, measured at 725 nm, grows-in after the excitation pulse with a lifetime of 310 ± 20 ps before decaying with a lifetime of 3.4 ± 0.1 ns. Direct excitation into the Bodipy chromophore at 635 nm gives rise to a similar decay lifetime ($\tau_S = 3.3 \pm 0.1$ ns) but eliminates the slow growth of the signal (Figure S4). From these various observations, we determine k_{EET} to be $3.1 \pm 0.2 \times 10^9\,\text{s}^{-1}$ for DPP-C_P-BOD.

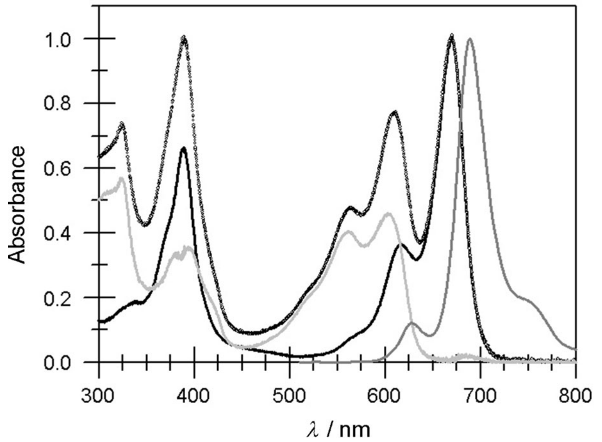

Figure 1. Absorption (open circles) and fluorescence ($\lambda_{EX} = 520$ nm, dark grey curve) spectra recorded for DPP-C_P-BOD in MTHF and comparison with the normalized absorption spectrum of the isolated acceptor, A (black curve). The difference between the two absorption curves (light grey curve) corresponds to the absorption spectrum of the donor, D.

This measured k_{EET} can be compared with that calculated from spectroscopic data recorded under the same conditions. On the basis of the ideal dipole approximation,[5] Equation (1) becomes valid and relates the rate constant to the spectral overlap integral ($J_F = 3.1 \times 10^{-4}$ cm) and the electronic coupling matrix element (V_{CO}) for coulombic interactions. Calculation of this latter term [Eq. (2)] requires knowledge of the transition dipole moments for donor ($\mu_D = 8.30$ D) and acceptor ($\mu_A = 10.42$ D), obtainable from analysis of the corresponding absorption spectral profiles for the lowest-energy transitions,[18] the average separation distance between centers of transition dipole moment vectors on donor and acceptor ($R_{CC} = 35.8$ Å), and the solvent screening factor, *s*. For MTHF at RT, and allowing for the Onsager cavity effect,[19] $s = 0.61$. The remaining term, κ, in Equation (2) is associated with the orientation factor describing alignment of transition dipole moment vectors[5] on donor and acceptor, which for the lowest-energy conformation has a modulus of 0.54. As such, the calculated value for k_{EET} becomes $3.5 \times 10^9\,\text{s}^{-1}$, which is in good agreement with the experimental data outlined above. Thus, for the linear DPP-C_P-BOD, and at a separation of about 36 Å, agreement between calculated and observed rates is surprisingly good. Such behavior has been noted previously for related dyads based on the *para*-carborane bridge.[7,20]

$$k_{EET} = \frac{2\pi}{\hbar} |V_{DA}|^2 J_F \tag{1}$$

$$V_{CO} = \frac{\mu_D \mu_A}{4\pi\varepsilon_0} \frac{s\kappa}{R_{CC}^3} \tag{2}$$

It seems instructive to examine if the extended dipole or atomistic models improve this agreement. Now, the line dipole approximation[9] replaces κ with two electronic charges for donor ($Q_D = \pm 0.76\,\text{D}\,\text{Å}^{-1}$) and acceptor ($Q_A = \pm 1.11\,\text{D}\,\text{Å}^{-1}$), assumed to represent a linear dipole covering the respective chromophore of length *L*, where scaling of the charges is provided by imposing the condition that $\mu_D = Q_D L_D$. This gives a set of four charges each separated by a mutual distance (d_{DA}) derived from the molecular model (Figure S1). The overall coupling element V_{XD} can now be

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obtained from Equation (3). Although this approach overcomes the tedious process of extracting details for the alignment of planes on the reacting subunits, it leads to an unacceptably low estimate for the rate constant ($k_{\mathrm{EET}} = 5.7 \times 10^8\ \mathrm{s}^{-1}$) which cannot be improved by minor adjustment of the structural parameters. The problem here is that whereas a linear transition dipole moment vector accurately reflects the donor it is a poor descriptor of the acceptor. Replacing the single vector with two identical linear lines of 4.7 Å (Figure S5), with correspondingly smaller charges, overcomes this problem and gives rise to an increased rate constant ($k_{\mathrm{EET}} = 2.8 \times 10^9\ \mathrm{s}^{-1}$) that fits nicely with experiment. Further refinement (V_{AT}) becomes possible by replacing the line dipoles with charges resident on each atom ($Q_{i,j}$),[10] as derived from quantum chemical calculations made by TD-DFT with the B3LYP functional and 6-31G basis set.[20] In this case, after scaling the summed atom charges to match μ_{D} and μ_{A} [Eq. (4)], we obtain $k_{\mathrm{EET}} = 3.0 \times 10^9\ \mathrm{s}^{-1}$. Agreement between calculated and observed values is now well within experimental error and most of the above problems are eliminated.

$$V_{\mathrm{XD}} = \frac{Q_{\mathrm{D}} Q_{\mathrm{A}}}{4\pi\varepsilon_0}\left[\frac{1}{D_{11}} + \frac{1}{D_{22}} - \frac{1}{D_{12}} - \frac{1}{D_{21}}\right] \tag{3}$$

$$V_{\mathrm{AT}} = \sum_{i=1} \sum_{j=1} \frac{Q_i^{\mathrm{D}} Q_j^{\mathrm{A}}}{R_{ij}} \tag{4}$$

It appears that intramolecular EET along the molecular axis in the linear DPP-$\mathrm{C_P}$-BOD can be well described by conventional theory without recourse to consideration of minor structural perturbations.[7,21] In fact, we can suppose that the molecular conformation is dynamic with respect to both length and alignment but these variations seem not to perturb the calculation. Indeed, dampening out any geometry changes by cooling to 80 K or by application of high pressure (< 550 MPa) have marginal effects on the rate of EET. The main effects of low temperature and high pressure are to force the thiophene appendages, most notably on the acceptor unit, to adopt a linear alignment with the central core of the chromophore. This effect is apparent from the reversible red shifts noted for emission spectra (Figure S6). It is also notable that excited-state deactivation of the Bodipy residue is thermally activated; a fact confirmed by temperature dependence studies made for direct excitation. However, critical examination of the ratio of donor/acceptor fluorescence yields for DPP-$\mathrm{C_P}$-BOD and an equi-molar mixture of the control compounds shows that the probability of EET is unaffected by changes in temperature or pressure.

The corresponding *ortho*-bridged dyad, DPP-$\mathrm{C_O}$-BOD, has the terminal chromophores in closer proximity, with the center-to-center separation reduced to 18.6 Å. The absorption spectrum is unaffected by this change while the photophysical properties of the Bodipy unit under illumination at 635 nm remain as above. Following preferential excitation into the donor at 525 nm, the fluorescence spectrum shows a small contribution from DPP ($\lambda_{\mathrm{FLU}} = 628$ nm) that amounts to about 4 % of the total signal (Figure S7). Excitation spectra (Figure S8) confirm highly efficient EET from DPP to Bodipy in MTHF.[17] Time-resolved fluorescence spectroscopy indicates that the lifetime of the donor unit is reduced to 49 ± 4 ps and that most of the emission associated with the acceptor grows-in after the excitation pulse with a lifetime of 55 ± 5 ps (Figure S9). The lifetime of the acceptor unit remains at 3.2 ± 0.1 ns following EET across the molecule. On this basis, k_{EET} for DPP-$\mathrm{C_O}$-BOD is $1.9 \pm 0.2 \times 10^{10}\ \mathrm{s}^{-1}$. Clearly, the rate of EET is faster for the *ortho*-bridged dyad, while the probability for EET exceeds 95 %.

Within the confines of the Förster ideal dipole approximation,[5] the modulus of the orientation factor κ can be derived from the energy-minimized molecular conformation (Figure S1) as being 0.27. Using this value in Equation (1), with the distance between the centers of the transition dipole moment vectors being 19.0 Å, leads to an estimate for k_{EET} of $3.9 \times 10^{10}\ \mathrm{s}^{-1}$. This value is twice the experimental rate constant and serves to indicate that the parameters derived from the computed structure are less successful at reproducing the observed rate constant for the *ortho* derivative. Even so, agreement between observed and predicted rate constants is reasonable and the two values merge if the separation distance is increased by only 2 Å. It is also questionable if the ideal dipole approximation is valid under these conditions where the closest contact between the reactants is much less than the center-to-center distance, unlike the case for the *para* derivative. Moving to the Kuhn extended dipole model,[9] using the revised parameters employed successfully for the linear dyad, gives a calculated k_{EET} of $2.6 \times 10^{10}\ \mathrm{s}^{-1}$. In this case, the extra effort expended on the calculation is well worthwhile and brings the computed value into very good agreement with the observed rate. This level of agreement is improved further by moving to the atomistic approach[10] ($k_{\mathrm{EET}} = 2.2 \times 10^{10}\ \mathrm{s}^{-1}$) and using the individual charges determined earlier. It appears that this method, although time consuming, solves many of the problems inherent to the ideal dipole approximation.

It is instructive to consider if there are underlying reasons why these carborane-derived dyads are suitable for interrogation by the Coulombic mechanism. Firstly, there is no suggestion that the carborane cluster acts as a conduit for through-bond electron exchange and, therefore, the main competing mechanism vanishes. Secondly, the organic connectors are short and fairly rigid. Only the bridging ethyne units are susceptible to out-of-plane bending modes that would perturb the geometry.[22] Rotations around these bridging linkages, which are inevitable under ambient conditions, do not impose significant changes on the orientation factors or separation distances. There are uncertainties about the exact magnitude of the screening factor[23] but the transition dipole moments, which are crucial parameters in this treatment, can be determined accurately without complications from upper excited states.

To further probe any conformational artefacts, EET in the *ortho*-carborane was studied as a function of temperature and applied pressure (Figure 2). On both cooling and at high pressure, emission from the acceptor is red shifted due to increased planarity along the molecular backbone. This effect has a small influence on the size of J_{F} but there are no significant changes in the probability of EET. During the pressure run, Φ_{F} decreases for the acceptor in line with the

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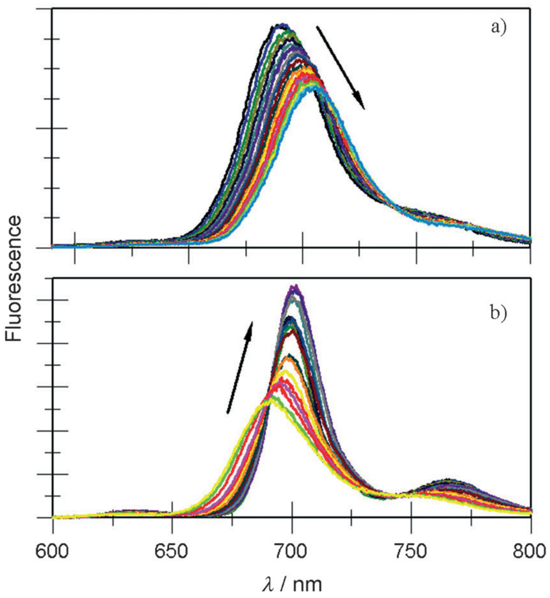

Figure 2. Effect of a) applied pressure (equal increments from 1 atm to 550 MPa) and b) temperature (equal decrements from 290 to 80 K) on the fluorescence spectrum recorded for DPP-C_O-BOD in MTHF. Excitation is at 520 nm.

energy-gap law but, according to control experiments made with A, emission is activated at ambient temperature. As such, cooling the solution leads to a small increase in Φ_F for the acceptor.

As a final check of the applicability of the coulombic mechanism to these systems, EET in the directly linked derivative, DPP-BOD, was examined in MTHF. Computer models constructed for this analogue are consistent with a center-to-center separation distance of 15.5 Å and, as for DPP-C_P-BOD, the dyad is linear. Here, absorption spectroscopy indicates that close positioning does not introduce electronic interactions between the terminals (Figure S10). Steady-state fluorescence spectroscopy shows that emission from DPP is barely resolvable from the background following excitation at 525 nm while fluorescence from the acceptor completely dominates the spectral profile (Figure S7). Excitation spectra (Figure S11) confirm the occurrence of highly efficient intramolecular ETT,[17] for which the probability exceeds 98%. Under direct illumination into Bodipy at 635 nm, $\Phi_F = 0.31 \pm 0.02$ and $\tau_S = 3.2 \pm 0.1$ ns such that close connection to the donor does not perturb the photophysical properties. It is more difficult to make the same assertion for fluorescence from the DPP-based donor, because of the low yield, but there are no obvious indications for electronic perturbation by the proximal acceptor. Fluorescence from the donor, under excitation at 525 nm, was too short-lived ($\tau_S <$ 25 ps) to be monitored by time-correlated, single-photon counting.

Improved temporal resolution was achieved using up-conversion fluorescence spectroscopy with 420 nm excitation, where the donor absorbs about 70% of incident photons. Under these conditions, emission from the DPP unit decays with a lifetime of 2.2 ± 0.2 ps while there is a concomitant growth in fluorescence of the Bodipy acceptor with a lifetime of about 2.3 ± 0.3 ps (Figure 3). This purported timescale for intramolecular EET resembles that expected for vibrational relaxation[24] but the close agreement between the two measurements is fully consistent with rapid EET across the molecule. On this basis, the experiment k_{EET} value is considered to be $4.4 \pm 0.4 \times 10^{11}$ s^{-1}.

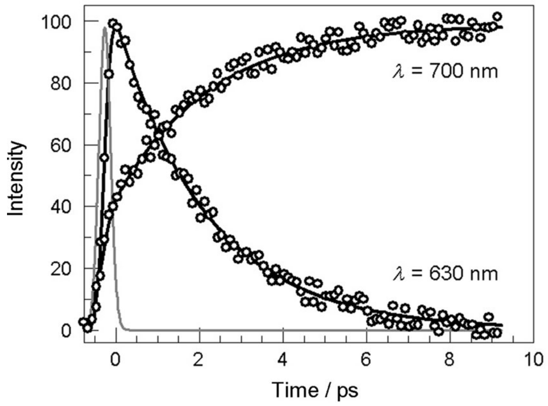

Figure 3. Time-resolved emission curves recorded for DPP-BOD following excitation at 420 nm; gaussian instrument response function (grey curve), data points shown as open circles and fits are shown as solid black lines.

Calculations made for DPP-BOD in MTHF at RT indicate that the distance separating the centers of the transition dipole moment vectors is 16.7 Å while the modulus of the orientation factor takes on a value of 0.34. These values lead to an estimate for k_{EET} of 1.3×10^{11} s^{-1} according to the ideal dipole approximation.[5] Following the trend established above, the revised Kuhn model[9] raises k_{EET} to 2.3×10^{11} s^{-1} while the atomistic model[10] brings k_{EET} to 2.8×10^{11} s^{-1}. All these derived rate constants are considered to be in good accord with experiment, even the ideal dipole approximation. Clearly, the Kuhn[9] and atomistic[10] approaches improve the agreement but not unduly. In the latter case, which has to be the recommended protocol to use with molecular dyads, the calculation underestimates the experimental rate constant by a factor of about 2-fold. This could be a consequence of competitive electron-exchange interactions,[25] given the short separation and the conjugated nature of the linkage. Indeed temperature dependence studies carried out with DPP-BOD in MTHF indicate that EET is weakly activated, after due allowance for temperature effects on the photophysics of the terminals. As such, EET is considered to involve a mixture of through-space and through-bond mechanisms in this particular case (see the Supporting Information and Figure S12 for details).

The main conclusion to emerge from this work is that k_{EET} can be calculated with good accuracy for large molecular dyads provided the connecting framework does not actively promote electron-exchange interactions. Rate constants for through-space EET calculated from the ideal dipole approximation agree to within a factor of 2-fold with experimental values but the molecular topology has to be taken into account. Treating the dipole as an extended line, or maybe a curve, improves the fit but not as well as using atomistic

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charges. This latter approach works extremely well for the target dyads. We expect to further challenge this protocol using dyads where the separation is reduced to about 12 Å.

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