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Characterization of a New Electron Donor-Acceptor Dyad in Conventional Solvents and Ionic Liquids

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Abstract

Ionic liquids are being tested as potential replacements for current electrolytes in energy related applications. Electron transfer (ET) plays a central role in these applications, making it essential to understand how ET in ionic liquids differs from ET in conventional organic solvents and how these differences affect reaction kinetics. A new intramolecular electron donor-acceptor probe was synthesized by covalently linking the popular photo-acceptor coumarin 152 with the donor dimethylaniline to create the dyad "C152-DMA" for potential use in probing dynamical solvent effects in ionic liquids. Molecular dynamics simulations of this dyad show considerable conformational flexibility of the linker group, but over a range of geometries in which the ET rate to vary minimally for times >100 ps. Steady-state and time resolved fluorescence methods show the spectra of C152-DMA to be highly responsive to solvent polarity, with ET-rates varying over the range $10^8 - 10^{12}$ s⁻¹ between nonpolar and high-polarity conventional solvents. Sensitivity to hydrolysis in the presence of acidic impurities limits the dyad's use to ionic liquids of high purity. Results in the few ionic liquids examined here suggest that, in addition to solvent polarity, electron transfer in C152-DMA also depends upon solvent fluidity and/or solvation times.

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I. Introduction

By virtue of its ubiquity in chemical and biological reactions, and its relevance in energy capture and storage applications, electron transfer has been a perennial interest in many areas of science and technology.¹⁻² Among the myriad ways researchers have sought to obtain a fundamental understanding of electron transfer rates and how one might control them, studies of covalently linked electron donor-acceptor (D-A),³⁻⁵ donor-bridge-acceptor molecules (D-B-A),⁶⁻¹¹ and more complex artificial photosynthetic systems¹²⁻¹⁴ have played a prominent role. The present report describes the synthesis and photophysical characterization of new intramolecular electron transfer probe intended for studies of the effects of solvation dynamics on electron transfer in ionic liquid and conventional solvents.

This new probe (Scheme 1) is constructed by covalently linking the coumarin 152 (C152) fluorophore, which acts as the photo-excited electron acceptor, to a dimethylaniline (DMA) donor via single methylene bridge. The C152 + DMA combination is one of the most commonly used pairings in studies of bimolecular electron transfer, and it has already been thoroughly characterized in conventional organic solvents,¹⁵⁻¹⁶ ionic liquids,¹⁷⁻²⁰ micelles and other complex environments,^{18, 21-22} and in neat liquid DMA.²³⁻²⁵ The C152-DMA construct shown in Scheme 1 represents an intermediate case between strongly coupled D-A pairs linked by a single bond that provides strong electronic coupling and ultrafast electron transfer, and D/A pairs connected by more extended bridges, for which much weaker coupling leads to reaction in the nanosecond and microsecond range. It was hoped that the simple linkage of the C152-DMA pair used here would provide an example of electron transfer occurring on time scales comparable to that of bimolecular C152/DMA pairs at first-solvation shell separations. While this hope was largely fulfilled, we also found that the C152-DMA dyad has one serious flaw for use in ionic liquids. The linkage between the 7-amino group of the coumarin ring and the DMA readily dissociates in the presence of trace amounts of acidic impurities, impurities difficult to completely remove from many ionic liquids. Nevertheless, this probe is suitable for use in a wide range of conventional solvents and some ionic liquids, making it useful for many purposes, if not for wide-ranging studies of ionic liquids. For this reason, the synthesis and photophysics of the C152-DMA dyad are reported herein, after briefly describing some of the prior work on bimolecular and intramolecular electron transfer in ionic liquid to which the present results will be compared.

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Over the past decade, many groups have investigated basic the physical chemistry of ionic liquids as reaction media, focusing on discerning how solvation in a purely ionic environment changes reactive processes compared to that present in conventional high-fluidity solvents, including studies of both bimolecular^{16-18, 20, 26-38} and intramolecular³⁹⁻⁵⁴ electron transfer. Studies of bimolecular electron transfer in ionic liquids have thus far uncovered a number of distinctive effects. The earliest of these studies compared reaction rates in ionic liquids and conventional solvents against simple predictions for diffusion-controlled rates.^{17, 26-29} As anticipated, the high viscosities of ionic liquids lead to slower rates compared to conventional solvents. However, in many cases reactions were found to be 10-100 times faster than expected based on viscosity alone.³⁰ This apparent rate acceleration was shown to be the result of two compounding effects: enhanced rates of diffusion of neutral solutes in ionic liquids⁵⁵ combined with the fact that stationary reaction conditions are often not achieved in the fluorescence quenching experiments typically used to measure rates.³⁰⁻³¹ In more recent work, a number of groups have measured the rates of electron transfer quenching of coumarin dyes by aromatic amines in ionic liquids and observed an apparent Marcus turnover in the rate at smaller than expected values of the driving force.^{18, 20, 32-33} Similar results were also reported in micelles and other slowly relaxing media,^{21-22, 56-58} and attributed to reduction of the effective reorganization energy due to the slow environmental response in these media. The validity of this interpretation has been questioned^{16, 34} and is currently still being debated.^{20, 35-36} In very recent work, Wu et al.³⁷⁻³⁸ employed a detailed model of the reaction-diffusion problem to analyze data a range of fluorophore/quencher pairs and concluded that some new feature was leveling reaction rates in ionic liquids in a way that is not apparent in conventional solvents. They proposed the slow reorientation of contact pairs gates reaction in ionic liquids in a manner that is unimportant in highly fluid solvents. Much has been learned from these studies of bimolecular electron transfer reaction. Nevertheless, disentangling the diffusional portion of reaction from the "intrinsic" electron transfer process in contact pairs remains subject to considerable uncertainty.

To focus on the solvent influence over the electron transfer event itself, a number of groups have therefore turned to measurements of electron transfer rates between chemically bonded donor/acceptor (D/A) pairs in ionic liquids.³⁹⁻⁵⁴ Most studies employed directly bonded D-A pairs linked by a single bond, and thereby having significant through-bond coupling. In such systems, electron transfer, or at least the achievement of the equilibrium extent of reaction,

is often observed to be much slower than in conventional solvents and to closely track solvation times.^{40, 49, 53-54} Surprisingly few studies have so far employed dyads with the weaker coupling produced by a more extended bridge between the donor and acceptor.^{47, 51-52} Of most relevance to the present work are the studies of Castner, Wishart and coworkers.⁵¹⁻⁵² They synthesized two dyads in which a coumarin dye was connected by one or two proline groups to the donor N,Ndimethyl-p-phenylenediamine, and compared the kinetics observed in acetonitrile to that in several ionic liquids. In the compound having a single proline bridge ("P1"),⁵⁷ electron transfer in acetonitrile was found to be dominated by a single component with a time constant near 0.5 ns. In contrast, reactions in the ionic liquids were markedly nonexponential, exhibiting a distribution of time constants ranging between 0.1-10 ns. These researchers attributed the distributed character of the kinetics to the fact that solvation spans many time scales in ionic liquids.⁵⁹ Because much of the solvation response occurs on time scales comparable to or slower than reaction, substantial heterogeneity in electron transfer rates is produced.⁶⁰⁻⁶¹ Curiously. rather different behavior was observed in the case of the P2 dyad, linked by two proline units.⁵⁸ The P2 dyad showed decays having three well separated components in both acetonitrile and in the ionic liquid solvents, which the authors attributed to the presence of multiple conformations adopted by the diproline linker. Average rate constants of the P2 dyad were also not markedly different from those of the P1 dyad, presumably due to the ability of some P2 conformers to achieve close D/A separations.

The remainder of this paper describes the synthesis and photophysics of the C152-DMA dyad, hereafter referred to as simply "the dyad", characterized using molecular dynamics simulations and steady-state and time-resolved fluorescence spectroscopy in a variety of solvents. Data on the solvent-dependent photophysics of two reference chromophores, C152 and H152, shown in Scheme 1, are also reported.

II. Methods

A. Reagents and Materials

The C152-DMA dyad, 7-((4-(dimethylamino)benzyl)(methyl)amino)-4-(trifluoromethyl)-2Hchromen-2-one, was synthesized using the route outlined in **Scheme 2**. The reagents 4dimethylaminobenzaldehyde (cat. no. 1030580100), 3-aminophenol (98%, 100242), ethyl 4,4,4trifluoroacetoacetate (99%, E50205), iodomethane (ReagentPlus[®], 99.5%, 289566), ethanol (200

proof, E7023), hexane (anhydrous, 95%, 296090), *N*,*N*-dimethylformamide (ReagentPlus[®], \geq 99%, D158550), ethyl acetate (anhydrous, 99.8%, 270989), sodium borohydride (\geq 96% gas-volumetric, 71320), potassium carbonate (anhydrous, free-flowing, Redi-DriTM, ACS reagent, \geq 99%, 791776), sodium sulfate (ACS reagent, \geq 99.0%, anhydrous, granular, 239313), zinc chloride (99.999% trace metals basis, 229997), and hydrogen bromide (ReagentPlus[®], \geq 99%, 295418) were used as received from MilliporeSigma (St. Louis, MO).

Preparation of 4-dimethylaminobenzyl alcohol (2): 1.0 g of 4-dimethylaminobenzaldehyde (1) was dissolved in 10 mL of ethanol, followed by the slow addition of 0.279 g (1.1 equiv) of NaBH₄ over the course of 10 minutes. The reaction mixture was stirred for 2 h at room temperature and monitored by TLC. The solvent was evaporated under reduced pressure followed by addition of water and extraction with ethyl acetate. The organic phase was treated with brine and dried over NaSO₄. The ethyl acetate was removed on a rotary evaporator to afford 4-dimethylaminobenzyl alcohol, which was subsequently used for the next step without any further purification.

Preparation of 4-dimethylaminobenzylbromide hydrobromide (**3**): 3.5 mL of 48% HBr was added to a pressure tube containing 0.5 g of 4-dimethylaminobenzyl alcohol (**2**). The tube was tightly sealed and the reaction stirred while heating for 2 h at 120 °C. The reaction was allowed to cool to room temperature and water then removed via rotary evaporation under reduced pressure to afford crude product (brown oil) which was used without additional purification.

3-Methylaminophenol (**5**) was synthesized from 3-aminophenol (**4**) following a literature procedure (yield: 68%).⁶²

Preparation of H152 (6): To generate the coumarin fluorophore by reaction of a phenol with a β -keto ester (i.e., Pechmann condensation), 1.34 g of 3-methylaminophenol (5) was dissolved in 20 mL of ethanol, followed by the addition of 2.20 g (1.1 equiv) of ethyl 4,4,4-trifluoroacetoacetate plus 1.78 g (1.2 equiv) of ZnCl₂. This mixture was refluxed for 12 h. The reaction mixture was cooled to room temperature and poured into 104 mL of 0.1 N HCl solution. The crude product was filtered, washed with water, and dried overnight. The crude product was further purified using a silica gel column eluted with a 3:1 (v/v) hexane–ethyl acetate solvent system under gravity (yield: 47%).

¹H NMR (500 MHz, DMSO) of **6**: δ 7.832 (1H, d), 7.099 (1H, q), 6.678 (1H, dd), 6.483 (1H, d), 6.450 (1H, s), 2.775 (3H, d). ¹³C NMR (125 MHz) of **6**: δ 159.42, 156.91, 154.07, 140.61, 140.36, 140.11, 139.11, 125.28, 123.08, 120.89, 118.70, 111.38, 107.28, 107.24, 101.59, 96.33, 29.11.

Synthesis of the C152-DMA Dyad (7): In a round bottom flask, 0.243 g of **3** was dissolved in 5 mL of acetone, neutralized with 0.125 g of K_2CO_3 (1.1 equiv), and stirred for 5 min. This reaction mixture was added to a 25 mL round bottomed flask equipped with a magnetic stirring bar, followed by the addition of 0.200 g of **6** (1.0 equiv) plus another 0.125 g of K_2CO_3 in 10 mL of DMF. The reaction was stirred for 2 days at room temperature. The reaction was filtered and the solvent removed via rotary evaporation (1 mmHg, 70 °C) over 8 h. The crude solid was purified using flash column chromatography by eluting with trimethylamine–hexane–ethyl acetate in a 2:29:69 (v/v/v) ratio (yield: 53%). The dyad was found to be highly susceptible to cleavage of the amine linkage in the presence of trace acid.

¹H NMR (500 MHz, DMSO) of **7**: δ 7.426 (d, 2H), 7.046 (d, 2H), 6.886 (d, 1H), 6.707 (d, 1H), 6.685 (d, 1H), 6.501 (s, 1H), 4.603 (s, 2H), 3.314 (s, 3H), 2.844 (s, 6H). ¹³C NMR (125 MHz) of **7**: 159.33, 156.25, 152.55, 149.64, 139.92, 127.54, 125.31, 124.52, 123.02, 120.83, 112.55, 110.27, 101.73, 98.14, 54.33.⁶²

Coumarin 152 (7-dimethylamino)-4-(trifluoromethyl)coumarin, CAS# 53518-14-2) was purchased from Exiton and used as received.

Solvents for spectroscopic measurements were HPLC grade acetonitrile and methanol (OmniSolv), spectroscopic grade ethylene glycol, dimethyl sulfoxide, propylene carbonate, tetrahydrofuran, 1,4-dioxane, toluene, and cyclohexane (Sigma-Aldrich), and methyl acetate (Fluka). Series of two solvent mixtures, cyclohexane/tetrahydrofuran (CHEX/THF) and cyclohexane/dibutyl ether (CHEX/DBE), were made volumetrically and compositions reported as volume fraction, assuming incompressibility. All conventional solvents were tested for water content using a Karl Fischer titrator. If the water content was less than 100 ppm, the solvent was used as received. Otherwise, solvents were dried with molecular sieves overnight. Samples were purged with nitrogen for three minutes before any experiments to prevent quenching by dissolved O₂. Absorption and emission spectra were recorded for each solvent to confirm lack absorbing impurities and minimal fluorescence in the visible region. Ionic liquid solvents 1-

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butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide ($[Pr_{41}][Tf_2N]$), methyltrioctylammonium bis(trifluoromethylsulfonyl)imide ($[N_{8881}][Tf_2N]$), and trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide ($[P_{14,666}][Tf_2N]$) were purchased from IoLiTec having stated purities of 98% but selected for high optical quality. These ionic liquids were purified using the methods described in previous work⁶³ in order to minimize impurity emission overlapping with the S₀-S₁ absorption band of the solutes.

B. Spectroscopic Methods

Steady State Absorption and Emission: All steady state absorption measurements were made in Parafilm-sealed 1-cm path length quartz cuvettes on a Hitachi UV-3010 UV-Vis spectrophotometer. Solvent spectra were measured and subtracted from all sample spectra. Fluorescence spectra were collected at 90° and 2 nm resolution using a SPEX Fluorolog 212 fluorimeter, calibrated with a set of emission standards using previously described methods.⁶⁴ Emission spectra were excited at 400 nm and collected over the range 410 - 700 nm. Fluorescence samples were also made in sealed 1 cm quartz cuvettes. Solute concentrations were chosen to provide optical densities at 395 nm of ~1.0 for absorption and ~0.15 for emission measurements.

Time Correlated Single Photon Counting (TCSPC): Time-correlated single photon counting (TCSPC) was used to measure lifetimes in the ns-ps range. Instrumental details can be found in previous work.⁶⁵ For the present experiments, excitation pulses were provided by the doubled output of a cavity-dumped Ti:Sapphire oscillator (Coherent Mira 900+PulseSwitch) tuned to 800 nm. All TCSPC samples were measured in sealed 1 cm quartz cuvettes. Emission decays at selected wavelengths (4 nm resolution) were collected in a 90° geometry at magic angle polarization. Stray excitation light was suppressed using a Kopp 3-73 filter. Use of a scattering sample showed the instrument response function (IRF) to be approximately 25 ps FWHM in all experiments.

Kerr-Gated Emission (KGE) Spectroscopy: For samples with decay times faster than 50 ps, time-resolved fluorescence spectra were collected using a Kerr-gated emission instrument, which was described in earlier work.⁶⁶⁻⁶⁷ Each sample was flowed through a 0.2 mm sample cell where it was excited with 388 nm pulses from the frequency doubled output of an amplified

Ti:Sapphire system (Coherent Verdi G18/Mira 900/RegA 9050). The emission spectrum between 408 to 699 nm was collected at each time step (-5 to 5 ps in steps of 100 fs, from 5 to 50 ps in steps of 200 fs, and from 50 ps to 300 ps in 2 ps steps) using an Acton SpectraPro-300i grating spectrograph and a liquid-nitrogen cooled CCD (1340 pixels, Princeton instruments). The FWHM of the fitted instrument response was approximately 400 fs. These experiments were performed in triplicate and the kinetic parameters averaged in producing the results reported. Deconvolution of the instrument response function from the spectra was accomplished using a global convolute-and-compare algorithm.⁶⁶⁻⁶⁷ Fits to log-normal functions were made after deconvolution to quantify the spectral dynamics.

Temperature Control: Most of the experiments were performed at room temperature, 293 ± 1 K. Steady state fluorescence and TCSPC measurements in ionic liquids were also performed over a range of temperatures between 213 - 353 K. For temperatures above 273 K, regulation was achieved using water from a recirculating water bath flowing through a brass cuvette holder. For lower temperatures, an Oxford variable temperature liquid nitrogen cryostat (model DN1754) was used. All samples were equilibrated at each temperature for at least thirty minutes prior to data collection.

C. Computational Methods:

Molecular dynamics simulations of the dyad in vacuum and acetonitrile (ACN) solution were performed using the GROMACS 2018.1 package⁶⁸ and the GAFF force field.⁶⁹ Atomic charges were obtained from a CHELP⁷⁰ fit of the electrostatic potential generated from an optimized structure at the B3LYP/6-311G++ level using the Gaussian09 package.⁷¹ Charges on equivalent atoms were symmetrized following the CHELP fit. Topology files were generated using AmberTools17⁷² and the *acpype* program.⁷³ Simulations in ACN consisted of one dyad molecule and 2450 ACN molecules in a ~6 nm cubic box with cubic periodic boundary conditions. Integration was carried out using the Verlet leapfrog algorithm with a step size of 2 fs. The particle-mesh Ewald method⁷⁴ was used to handle the long-range electrostatics and non-bonded interactions were calculated using a Verlet neighbor list with a 1.4 nm cutoff. The P-LINCS algorithm was used to constrain all hydrogen-containing bonds.⁷⁵ The same methods were applied to simulate behavior in the gas phase simply by omitting the ACN molecules.

Following a short energy minimization procedure, the simulation box was equilibrated

using three consecutive 500 ps simulations in NVT, NPT, and NVT ensembles. The pressure of the NPT simulation was set to 1 bar and regulated using a Berendsen barostat with a relaxation time of 5 ps, whereas the temperature was 293.15 K and regulated using a modified Berendsen thermostat with a relaxation time of 0.5 ps.⁷⁶ Production NVT simulations were then carried out for 50 ns with dyad coordinates saved every 0.1 ps, giving a total of 5×10^5 structures.

III. Results and Discussion

A. Molecular Dynamics Simulations

The methylene linkage chosen to connect the donor and acceptor groups might be expected to lead to significant intramolecular flexibility in the C152-DMA dyad. To assess the conformations present in the ground state, two approaches were used. First, attempts were made with the conformational search algorithms available in MacroModel 11,⁷⁷ followed by DFT calculations of selected conformers. However, it became clear from such calculations that the dyad structure near room temperature is not adequately described by a small number of well-defined conformers. For this reason, classical MD simulations were performed both in acetonitrile and the gas phase to provide more appropriate sampling of conformational space.

Three dihedral angles, defined in **Figure 1(a)**, were used to coarsely specify the geometries of the dyad observed in these simulations. Several representations of the distributions observed for these three angles are shown in **Figures 1(b,c)** and **Figure 2**. There are eight heavily populated regions in this conformational space, defined by population minima approximately located by planes at $D1 = \pm 90^{\circ}$, D2 = 0, and D3 = 0. For simplicity, if one uses the 2-fold rotational symmetry about D1 to fold populations into the range $-90^{\circ} \le D1 \le 90^{\circ}$, the four occupied regions of conformational space depicted in Figure 2 result. As shown by the representative structures in Figure 2, all four heavily populated regions involve structures in which the donor and acceptor aromatic planes are nearly orthogonal to one another. Comparison of the structures observed in the gas- and solution-phase simulations (Figure 1(b) and **Figure S3**) show them to be quite similar. The primary difference is that conformer distributions are slightly more localized in solution, particularly with respect to the D2 angle.

The time evolution of the three dihedral angles (**Figure S4**) shows that the dyad samples the conformational space within one of these four regions on a picosecond time scale and makes

transitions among regions on a much longer time scale. Specifically, in acetonitrile solution, fast fluctuations within each region are such that D1-D3 vary by $\pm 10-15^{\circ}$ (1 σ) when viewed in 10 ps windows. Transitions among conformer regions take place via ~180° jumps, which occur on average once every 0.7 ns. Interconversion among conformers is faster in the gas-phase, as might be expected given the absence of intermolecular friction. The remainder of this discussion will consider only the more relevant solution-phase results.

The presence of a distribution of conformers implies electron transfer will be initiated from a distribution of ground-state geometries. This geometric variability should result in distributions over the key parameters controlling electron transfer rates, namely the driving force, reorganization energy, and most importantly, the electronic coupling. Rather than attempt detailed quantum mechanical calculation of these quantities, two simple surrogates, the donoracceptor (center-of-mass) distance R_{DA} , and the angle θ_{π} between the aromatic planes of the donor and acceptor were monitored. In **Figure 3**(a, b) the distributions of these quantities are plotted as the blue curves. Average values are $R_{DA} = 0.80 \pm .08$ nm and $\theta_{\pi} = 90 \pm 23^{\circ}$ (1 σ). These averages, and the way that R_{DA} and θ_{π} are distributed, are remarkably similar in all four of the conformer regions, as shown in **Figure S5**. Thus, it seems reasonable to conclude that the existence of these four slowly interconverting populations of conformers will have little effect on the electron transfer kinetics observed. However, the variations of R_{DA} and θ_{π} within each region are not small and may be expected to give rise to distributed electron transfer kinetics.

To examine this possibility further, the main effect on electron transfer kinetics is assumed to result from geometric variations modulating the electronic coupling, modeled as functions of θ_{π} and R_{DA} using the model function $k_{ET} \propto \cos^2 \theta_{\pi} \cdot \exp(-\beta R_{DA})$. The electron coupling decay contant β is assumed to have a value of 15 nm⁻¹, a value typical of condensed media.^{30, 78} The dashed red curves in Figure 3 show how these model dependences samples the distributions of conformer geometries. In both cases, the largest values of k_{ET} come from regions well removed from the most probable conformations. Taking the R_{DA} and θ_{π} variations separately and correlating fluctuations in $\exp\{-\beta R_{DA}(t)\}$ and $\cos^2 \theta_{\pi}(t)$ over the course of the simulation leads to the normalized time correlation functions shown in panels (c) and (d). These functions both decay rapidly, with correlation times of ~5 ps. These times suggest that the distribution of conformers present in C152-DMA should not lead to distributed kinetics for

reactions taking place on time scales of 100 ps or more. For such reactions, homogeneous kinetics of the geometrically averaged structures is expected. For faster reactions, some distributed character and perhaps gating of reaction by conformational fluctuations are anticipated.

B. Steady-State Characterization

Steady-state absorption and emission spectra of the dyad and the reference chromophores C152 and H152 were measured in a variety of solvents and solvent mixtures to characterize their polarity dependence. Relevant data are summarized in **Table S1**. We note that whereas several solvatochromic studies of C152 have already been reported,⁷⁹⁻⁸¹ no such information is available for H152.

Figure 4 compares absorption and emission spectra of these three solutes in the nonpolar solvent cyclohexane and the highly polar solvent acetonitrile. In cyclohexane, the spectra of all three molecules exhibit similar vibronic structure, and their absorption and emission spectra are offset by comparable Stokes shifts. In acetonitrile, all spectra are broadened, and the Stokes shifts are increased by solvation, but the similarities in spectral shape among the three are maintained. These similarities suggest that the coumarin aromatic system is the absorbing chromophore in all three cases, and that excitation of the dyad leads to a locally excited (LE) state similar to those of other 7-amino substituted coumarins.⁸² Because the frequencies of the and chromophore redox properties of the dyad are expected to be closer to those of C152, we will use C152 as a reference for the photophysics expected in the absence of electron transfer.

Absorption and emission spectra of the dyad in solvents having a range of polarities are shown in **Figure 5**. As solvent polarity increases, both the absorption and emission spectra red shift and broaden. The emission shifts are considerably larger, due to the well-known increase in dipole moment in S_1 compared to S_0 , characteristic of this type of coumarin. Similar solvent dependence is found for C152 and H152 (Table S1). One feature of the dyad emission of note is the increased noise observed in higher polarity solvents (MeAC and ACN in Figure 5). This noise reflects a roughly ~500-fold reduction in the dyad's fluorescence quantum yield with increasing solvent polarity. Such strong quenching is absent in C152 and H152 and is the first indication that the anticipated electron transfer is occurring in the dyad.

In Figure 6, absorption and emission frequencies of the dyad are compared to those of

C152. The excellent correlations shown here underscore the similarity of the dyad LE state to the S_1 state of C152. However, whereas the transition energies of C152 and the dyad are linearly related, the slopes in Figure 6 (0.71 and 0.64) are not close to unity. These slopes indicate the dyad has only 2/3 of the solvent sensitivity of C152, which could be indicative of significantly reduced charge separation in the LE state compared to C152. However, further analysis of the solvatochromic data and electronic structure calculation indicate otherwise.

Estimates of the dipole differences between the absorbing (S₀) and emitting (S₁ or LE) states, $\Delta \mu = |\vec{\mu}(S_1) - \vec{\mu}(S_0)|$, were made using a Lippert-Mataga analysis of the Stokes shifts of all three solutes. Modeling the system as a solute consisting of a polarizable point dipole centered in a spherical cavity of radius *a* and the solvent as a dielectric continuum, such a model predicts

$$v_{\rm abs} - v_{\rm em} = (v_{\rm abs} - v_{\rm em})_{\rm gas} + \frac{2}{(4\pi\epsilon_0)h} \frac{(\Delta\mu)^2}{a^3} \Delta f.$$
 (1)

where Δf is the solvent orientational polarizability,

$$\Delta f = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} - \frac{n_D^2 - 1}{n_D^2 + 2}.$$
(2)

with ε_r the relative permittivity and n_D the refractive index of the solvent. Because the solutes examined here are not spherical in shape, there is no unambiguous way to assign an appropriate value of the cavity radius *a*. Previous work on the similar chromophore coumarin 153⁸³ showed that an effective cavity radius based on the van der Waals volume of the solute extended by 50%, to account for the average size of solvent layer, provided estimates of $\Delta \mu$ in line with electronic structure calculations and more definitive experiments. Adopting this approach, the slopes of the solvatochromic plots in **Figure 7** yield the dipole difference estimates in **Table 1**. Insofar as this choice of a_{eff} is reasonable, these estimates show the solvatochromic data are consistent with the charge shift between S₀ and the LE state of the dyad being similar to the S₁-S₀ difference in C152. The value of $\Delta \mu$ estimated for H152 is slightly smaller, as would be expected upon replacing an electron donating alkyl group on the amine with a hydrogen atom.

For comparison, Table 1 also lists dipole moments calculated at the CAM-B3LYP/6-311++G(d,p) level in the gas phase. Calculations of the dyad were performed on a number of representative conformers in optimized S_0 geometries, and the range of values for these conformers are tabulated. These calculations confirm minimal mixing between the DMA and coumarin portions of the molecule exists in either the S_0 or (vertical) S_1 /LE states, as well as the Page 13 of 40

similarity of the charge shift in the $S_0 \rightarrow S_1$ transitions of the dyad and C152. They also confirm the presence of a charge-transfer state of the dyad, as indicated by the large dipole moments of the vertical S_2 states of all conformers studied. The frontier molecular orbitals and some additional characteristics of the LE and CT states are provided in **Figure S6**.

C. Time-Resolved Measurements

Representative fluorescence decays of the dyad are shown in **Figure 8** and selected multiexponential fits are provided in **Table 2**. The decays in Figure 8 were all recorded using TCSPC, which has an instrumental response time of ~25 ps. Five of the highest polarity solvents, represented by acetonitrile (ACN) and methanol (MeOH) in Figure 8, have lifetimes shorter than 25 ps, and these solvents were also measured using Kerr Gated Emission (KGE) spectroscopy. Fits of the KGE data are compiled in Table 2B. Finally, emission decays of the reference chromophores C152 and H152 were measured in all solvents, and their lifetimes are also provided in Table 2.

With few exceptions⁸⁴ the decays of C152 and H152 are well described by single exponential functions. In contrast, in the case of the dyad, exponential or nearly exponential decays are only observed in some of the least polar solvents, for example cyclohexane (CHEX) and dibutyl ether (DBE) shown in Figure 8. In the majority of solvents, dyad emission is significantly non-exponential, requiring 3-4 components for accurate representation. In many solvents, the longest component has an amplitude of a few percent and a lifetime of several nanoseconds, close to that of H152 in the same solvent. In the highest polarity solvents, such as acetonitrile and methanol in Figure 8, this long component is readily distinguished, because it decays on a much longer time constant than all other components. These nanosecond tails are attributed to the presence of residual H152 impurity in the dyad samples. As discussed in the Supporting Information, H152 is both a precursor in the dyad synthesis and is produced by acidcatalyzed heterolysis of the dyad. In most solvents, the amplitude of this longest component is <5 %. When such a small and well-separated component was obtained from unconstrained fits, the TCSPC data were refit after constraining the lifetime of this component to be equal to the H152 lifetime. These constrained fits are what are reported in Table 2A, and when calculating average dyad lifetimes and rates, these putative impurity components are omitted.

Representative KGE data of the dyad in propylene carbonate are shown in Figure 9. With

the better time resolution of the KGE technique (~400 fs IRF), one observes the dyad emission to undergo a dynamic Stokes shift. The peak frequencies of these spectra could be fit with biexponential functions having times constants in the few picoseconds range. The average times of these shifts are reasonably correlated (R^2 =0.74, N=5) to the average times measured for the nonreactive solute coumarin 153.⁸³ As illustrated by the data in Figure 9(c), the time dependence of the peak height and integrated intensity of the emission are quite similar. In all cases, the intensity data could be represented by two primary components plus a slower component in the tens of picoseconds range having an amplitude of ≤6% (Table 2B). Due to the lower signal-tonoise and time range of the KGE experiment, the small (<3%) nanosecond components found in the TCSPC data of these solvents are not observed.

The non-exponential emission decays found for the dyad complicate description of the rate of electron transfer and its solvent dependence. Rather than attempt any detailed characterization of the distributed kinetics here, two limiting rate constants were extracted from the multi-exponential fits of the decay data. Using the lifetime of C152 (τ_{c152}) to estimate the dyad lifetime in the absence of electron transfer, the rate constants

$$k_{\rm ET}^{(1)} = 1/\langle \tau \rangle_{\rm dyad} - 1/\tau_{C152} \qquad \langle \tau \rangle_{\rm dyad} = \sum a_i \tau_i / \sum a_i \qquad (3)$$

and

$$k_{\text{ET}}^{(2)} = \langle k \rangle_{\text{dyad}} - 1/\tau_{C152} \qquad \langle k \rangle_{\text{dyad}} = \sum (a_i/\tau_i)/\sum a_i \qquad (4)$$

were calculated. The symbol Σ' in these equations indicates omission of small-amplitude (<6%) impurity components. One can view $k_{\text{ET}}^{(1)}$ and $k_{\text{ET}}^{(2)}$ as providing approximate lower and upper bounds to the distribution of rates present.

Before discussing these rates, it should be mentioned that C152 undergoes a twisted intramolecular charge-transfer (TICT) process in high polarity solvents.^{79-82, 85} It might be thought that this process would render C152 unsuitable as a lifetime reference for the dyad. This issue is discussed in detail in the Supporting Information (Section B) where it is shown that the effect of the TICT process should have a negligible effect on the ET rates reported here.

Figure 10 plots the observed rate constants versus the steady-state emission frequency of the dyad, $\langle v_{em} \rangle$, which is used here as a measure of effective solvent polarity. A similar correlation is found when these rates are plotted versus the dielectric measure of total solvent polarizability $(\varepsilon_r - 1)/(\varepsilon_r + 2)$, as shown in **Figure S8**. The filled symbols in Figure 10 are

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the logarithmic averages of $k_{\text{ET}}^{(1)}$ and $k_{\text{ET}}^{(2)}$, and the limits of the error bars serve to denote their individual values. Although there is considerable scatter and, in some cases a large difference between $k_{\text{ET}}^{(1)}$ and $k_{\text{ET}}^{(2)}$ in these data, a clear correlation exists between k_{ET} and $\langle v_{em} \rangle$ in most solvents. A substantial dependence of the electron transfer rate on solvent polarity of this sort is expected given the large difference in charge separation and thus dipole moments of the LE and CT states of the dyad (~20 D based on the calculations in Table 1). It seems reasonable to attribute the increasing rate with increasing solvent polarity as being primarily due changes in the reactive driving force, assuming that the electron transfer lies within the normal regime.

In a number of solvents, labeled in Figure 10, values of k_{ET} appear to be smaller than expected based on the relationship established by the majority of solvents. With the exception of toluene, these solvents all have much higher viscosities than do the remaining solvents. (See Table S1.) For example, the two ionic liquids near the bottom of the figure, [P_{14,666}][Tf₂N] and [N₈₈₈₁][Tf₂N], have viscosities >500 mPa s⁻¹ near room temperature, and in these solvents electron transfer is too slow to measure. (This situation persists even up to 350 K, as discussed in SI Section C.) These observations suggest that, in addition to polarity, some other factor such as solvent friction plays a role in determining the rate of electron transfer.

Support for friction being relevant to this reaction can be found in temperature-dependent TCSPC measurements of the dyad in the ionic liquid [Pr₄₁][Tf₂N], which are shown in **Figure 11**. Over the 25 K temperature range (278-303 K) the ionic liquid's polarity (as judged by $\langle v_{em} \rangle$) varies negligibly, whereas the viscosity decreases by nearly a factor of four and k_{ET} doubles. An Arrhenius analysis of the data, shown in the inset to Figure 11, yields an activation energy of 21 kJ/mol and a prefactor of 1.3×10^{14} s⁻¹. This prefactor is too high to be interpreted in terms of a reactive frequency in such a reaction. A more realistic description is a reaction which is nearly activationless but has a frictional prefactor proportional to viscosity, η^{-p} , with $p\sim$ 0.6. This dependence on solvent viscosity could either reflect some large-amplitude solute motion required for reaction, or a dependence on solvation time, which approximately tracks viscosity. As discussed in Section D of the Supporting Information, the present data are unable to distinguish between these two possibilities.

It is interesting to compare the electron transfer rates measured for C152-DMA dyad to the similar intramolecular dyads studied by Castner, Wishart and coworkers,⁵¹⁻⁵² which were

constructed from an aromatic amine donor and a coumarin 343 photoacceptor linked by one (P1) or two (P2) proline groups. Electron transfer in both the P1 and P2 molecules is much slower than observed for the C152-DMA dyad. Focusing on the simpler P1 dyad, ${}^{51-52}$ average rate constants calculated using Equations 3 and 4 provide values $(k_{ET}^{(1)} | k_{ET}^{(2)})/10^9 \text{ s}^{-1}$ of (1.6 | 2.8) in acetonitrile, (1.6 | 3.5) in methanol, and (0.73 | 1.4) in [Pr₄₁][Tf₂N] at 293 K. Comparison to Table 2 shows electron transfer in the C152-DMA dyad are 100-1000 times faster in the two conventional solvents and 10-40 times faster in the ionic liquid [Pr₄₁][Tf₂N]. Differences in both the electronic coupling and the redox properties of the donor and acceptor are likely responsible for the different kinetics in these two dyads. For example, the free energy change in the C152 + DMA bimolecular reaction in acetonitrile is estimated to be about -0.43 eV,¹⁵ and estimates for the C152-DMA dyad are not expected to differ appreciably from this estimate. In contrast, reaction free energies of the P1 and P2 dyads in acetonitrile were estimated to be -1.6 eV, ${}^{51-52}$ much more negative and the driving force much greater than in the C152-DMA dyad. The P1 and P2 dyads were thought to occur well within the Marcus inverted regime, whereas the C152-DMA reaction is more likely to fall within the normal regime in most solvents.

Comparison can also be made between the present results and rates measured for the equivalent bimolecular reaction between C152 and DMA. Most desirable for such a comparison are effective unimolecular reaction rates between C152 and a single proximal DMA molecule. The rate of this idealized process can be estimated from previously reported data only by making some significant assumptions. Fewest assumptions are required for interpreting the quenching dynamics of C152 in neat liquid DMA, which has been reported by two groups.²⁴⁻²⁵ Both groups reported quite similar bi-exponential fluorescence decays with initial rates ($k_{ET}^{(2)}$, Eq. 4) of ($2.0\pm.2$)×10¹² s⁻¹. Assuming reaction occurs between C152 and only one of the approximately 10 DMA molecules within its first solvation shell^{25, 37} acting independently, the rate constant for comparison to the dyad data is about 10-fold smaller, $k_{ET}^{(2)} \sim 2\times10^{11}$ s⁻¹. Measurements of concentrated DMA solutions, where most reaction is expected to occur between preformed ground-state C152/DMA pairs, also provide similar estimates. In solutions of >0.5 M DMA mixed with toluene,²⁵ chlorobenzene,²⁵ cyclohexane,⁸⁶ and two ionic liquids²⁰, one finds values of $k_{ET}^{(2)}$ in the range (1-5)×10¹¹ s⁻¹. In both the neat and mixed solvent cases, these effective unimolecular rate constants provide estimates of rates associated with reaction between a single

C152 + DMA contact pair averaged over relative positions and orientations of first solvation shell neighbors. The polarities of neat DMA ($\varepsilon_r = 5.0^{25}$) and these concentrated DMA mixtures are expected to fall roughly in the middle of the range studied, where rates measured for the dyad are closer to 10^{10} s⁻¹. Thus, the C152-DMA dyad appears to provide an example of an intramolecular electron transfer having electron transfer rates only slightly slower than average rates of contact pairs in the intermolecular process it was intended to mimic.

IV. Conclusions

This work documented the synthesis and photophysical properties of a new electron donor-acceptor dyad, C152-DMA, made by covalently linking the photo-acceptor C152 and the DMA donor via a single methylene bridge. Although the simple linker employed here confers significant conformational flexibility to the dyad, molecular dynamics simulations suggest that this flexibility only causes electron transfer rates to be distributed over a modest range.

Apart from the rapid fluorescence quenching caused by electron transfer, the absorption and emission characteristics of the C152-DMA dyad are very similar to those of the reference compounds C152 and H152, demonstrating weak substantial coupling between the S_0 and LE states of the dyad. The coumarin chromophore of the dyad and its references are all strongly solvatochromic, as are most 7-aminocoumarins.

Time-resolved emission of the dyad was found to be multi-exponential indicating a distributed character to the electron transfer reaction in most solvents. Conformational and solvation dynamics are likely contributors to this distributed character, especially in high polarity solvents where reaction occurs on the same time scales as both conformational relaxation and solvation. Average rate constants in conventional solvents are strongly dependent on solvent polarity. Rates are near 10^8 s⁻¹ in nonpolar solvents, increasing to $\sim 10^{12}$ s⁻¹ in the most polar solvents. This variation is most likely the result of the increasing driving force for charge separation with increasing solvent polarity. Absence of observable quenching in two high-viscosity ionic liquids, together with the temperature dependence observed in a low-viscosity ionic liquid, suggest that solvent friction also plays an important role in determining dyad electron transfer rates. Further study is needed to determine whether this frictional effect is due to a dependence on solvation times, as found in several other intramolecular cases^{40, 49, 53-54} or

perhaps due to the slowdown of conformational sampling with increasing viscosity.

The rates of electron transfer observed in the C152-DMA dyad are considerably faster than rates previously reported for the related coumarin - aromatic amine dyads studied by Castner, Wishart and coworkers.⁵¹⁻⁵² C152-DMA reaction rates appear to be closer to those between contact DMA + C152 pairs, estimated from intermolecular quenching experiments. The latter similarity suggests the C152-DMA dyad is an apt intramolecular analog of the bimolecular process. Although its sensitivity to acid-catalyzed hydrolysis limits its use to only highly purified ionic liquids, the C152-DMA dyad should nevertheless provide a useful new probe for comparisons between electron transfer in ionic liquids and conventional solvents.

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Supporting Information: Mechanism and illustration of the acid-catalyzed hydrolysis of the dyad; comparison of dyad and H152 lifetimes; dyad conformational distributions in the gasphase and acetonitrile; time dependence of the dyad dihedral angles D1-D3 in acetonitrile; distributions of dyad interplanar angle and donor-acceptor distance from different conformer regions; table of solvent properties and characteristics of the spectra of C152, H152, and the C152-DMA dyad; frontier orbitals and some properties of the LE and CT states of C152-DMA; lifetimes of C152, H152, and the dyad vs. dyad emission frequency; dyad electron transfer rate constants vs. total solvent polarizability; steady-state emission spectra of C152 and the dyad in $[P_{14,666}][Tf_2N]$; solvent viscosities, and emission frequencies of C152 and the dyad in $[N_{8881}][Tf_2N]$ and $[P_{14,666}][Tf_2N]$; table of fits to viscosity data in the ionic liquids; average lifetimes of C152 and the dyad in $[N_{8881}][Tf_2N]$ and $[P_{14,666}][Tf_2N]$; Estimated frictional component of k_{ET} versus viscosity and solvation time.

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Table 1: S ₁ -S ₀ Dipole Difference Estimates from Solvatochromic Analysis and DFT
Calculations

	A. Solvato	chromic A	nalysis	B. DFT Calculations					
solute	$\Delta v / \Delta f$ / 10 ³ cm ⁻¹	a _{eff} / Å	Δμ / D	μ(S ₀) / D	μ(S ₁) / D	μ(S ₂) / D	$ \Delta \vec{\mu}_{10} $ / D		
C152	3.08	5.43	$7.0 \pm .5$	7.79	13.23	11.21	5.53		
H152	2.43	5.28	$6.0 \pm .5$	7.45	12.48	10.93	5.10		
dyad	1.94	6.35	7.0±.9	8.6-11	13-17	30-39	5.6-6.6		

A. $\Delta v / \Delta f$ is the slope of the fit to Eq. 1.

B. Calculated values are from gas-phase CAM-B3LYP/6-311++G(d,p) calculations. Geometries were optimized for the ground state and excited-state values derived from TDDFT calculations at these S_0 geometries. For the dyad, a number of representative conformations were selected, and the range of values obtained from these conformers is tabulated.

Table 2: Multi-Exponential Representations of Dyad Emission Decays and ET Rate Constants

A. TCSPC Measurements

Solvent	a 1	a 2	a 3	84	τ ₁ / ps	τ2 / ps	τ3 / ps	τ4 / ns	τ H152 / ns	τc152 / ns	<τ> _{dyad} / ps	k _{et} ⁽¹⁾ / s ⁻¹	k _{et} ⁽²⁾ / s ⁻¹
Cyclohexane (CHEX)	1.00	-	-		3183		-		3.7	4.1	3183	6.9×10 ⁷	6.9×10 ⁷
50/50 vol% CHEX+DBE	0.22	0.77	-	0.02	21	1956	-	(3.9)	3.9	3.8	1531	3.9×10 ⁸	1.1×10^{10}
Dibutyl Ether (DBE)	0.21	0.78	-	0.01	529	1148	-	(4.1)	4.1	4.8	1014	7.8×10 ⁸	8.8×10^{8}
Toluene (TOL)	0.26	0.69	-	0.05	216	1091	-	(3.9)	3.9	4.4	855	9.4×10 ⁸	1.7×10^{9}
50/50 vol% CHEX+THF	0.83	0.16	-	0.01	63	170	-	(4.5)	4.5	4.7	81	1.2×10^{10}	1.4×10^{10}
1,4-Dioxane (DIOX)	0.59	0.36	0.05	0.004	32	135	477	(4.7)	4.7	4.9	92	1.1×10^{10}	2.1×10^{10}
Tetrahydrofuran (THF)	0.97	0.02	-	0.004	8	104	-	(4.8)	4.8	5.4	10	1.0×10 ¹¹	1.3×10 ¹¹
Ethylene Glycol (EG)	0.97	0.02	-	0.02	18	980	-	(4.4)	4.4	1.1	34	2.8×10^{10}	5.5×10^{10}
$[N_{8881}][Tf_2N] (N_{8881})$	0.093	0.91	-	-	1123	5001	-	-	5.1	4.8	-	<	<107
[P _{14,666}][Tf ₂ N] (P _{14,666})	0.10	0.90	-	-	1201	4921	-	-	4.8	4.5	-	<107	
$[Pr_{41}][Tf_2N] (Pr_{41})$	0.64	0.30	0.02	0.04	12	105	2138	(5.2)	5.2	3.4	88	1.1×10^{10}	5.8×10 ¹⁰

B. KGE Measurements

Solvent	a 1	a ₂	a 3	τ ₁ / ps	τ ₂ / ps	τ3 / ps	<τ> _{dyad} / ps	τ _{H152} /ns	τc152 / ns	kет ⁽¹⁾ / s ⁻¹	kет ⁽²⁾ / s ⁻¹
Methyl Acetate (MEAC)	0.47	0.49	0.04	0.3	1.9	42	2.2	5.0	4.8	1.5×10^{11}	2.2×10 ¹¹
Propylene Carbonate (PC)	0.56	0.40	0.05	0.4	2.3	39	3.0	5.5	2.0	3.4×10 ¹¹	1.9×10 ¹²
Dimethylsulfoxide (DMSO)	0.56	0.40	0.04	0.1	0.9	64	2.8	5.0	0.97	3.4×10 ¹¹	1.6×10^{12}
Acetonitrile (ACN)	0.39	0.55	0.06	2.0	10	50	3.6	5.4	2.1	3.5×10 ¹¹	4.2×10^{12}
Methanol (MeOH)	0.23	0.73	0.04	3.8	10	43	5.0	4.9	0.96	2.3×10 ¹¹	6.4×10 ¹¹

Fits are to the function $\Sigma_i a_i \exp(-t/\tau_i)$ with $\Sigma_i a_i = 1$. TCSPC decays were measured at the steady-state emission whereas the KGE fits show the average time dependence of the peak height and integrated intensity of the emission band. $\langle \tau \rangle_{dyad}$ is the average decay time of the dyad $\Sigma_i a_i \exp(-t/\tau_i)/\Sigma_i a_i$ where the prime denotes exclusion of component 4, which is assumed to be due to emission from H152 impurity. $k_{ET}^{(1)}$ and $k_{ET}^{(2)}$ are estimated rates of electron transfer calculated according to Eqs. 3-4.





Figure 1: (a) Dihedral angle definitions. (b) One-dimensional distributions of angles D1-D3 in acetonitrile (solid curves) and in the gas phase (dashed). (c) 2-dimensional distributions in acetonitrile. In both the 1d and 2d distributions the values shown are the numbers of occurrences out of 5×10^5 samples.



Figure 2: The most populated regions of conformational space shown as isosurfaces capturing 65% of the population. For clarity, values of $|D1| > 90^{\circ}$ here are folded into $-90^{\circ} \le D1 \le 90^{\circ}$ using the 2-fold rotational symmetry of the DMA group. The conformer regions designated 1-4 are defined by the planes D2 = 0 and D3 = 0. The molecular structures show representative geometries selected from the most populated areas within these four regions.



Figure 3: Distributions of (a) the center-of-mass distance between the donor and acceptor groups R_{DA} and (b) the angle between their aromatic planes, θ_{π} , observed in acetonitrile. The dashed red curves in these two panels indicate the approximate variation in electron transfer rates expected from these geometric parameters ($\beta = 15 \text{ nm}^{-1}$). (c) and (d) show the autocorrelation functions of R_{DA} and θ_{π} averaged over the 50 ns trajectories. The τ values indicated are the correlation times of these functions.



Figure 4: Normalized absorption and emission spectra of the dyad (black) and reference fluorophores C152 (red) and H152 (blue dashed) in cyclohexane and acetonitrile.



Figure 5: Normalized absorption (a) and emission (b) spectra of the dyad in selected solvents: cyclohexane (CHEX), dibutyl ether (DBE), toluene (TOL), 1,4-dioxane (DIOX), methyl acetate (MEAC) and acetonitrile (ACN).



Figure 6: Correlation of the average absorption and emission (b) frequencies of the dyad with those of C152. The regressions shown are: (a) $\langle v \rangle_{dyad} = 0.71 \langle v \rangle_{C152} + 7.29$ (*N*=24, *R*²=0.92) and (b) $\langle v \rangle_{dyad} = 0.64 \langle v \rangle_{C152} + 7.57$ (*N*=24, *R*²=0.95).



Figure 7: Lippert-Mataga plots of the Stokes shifts $\Delta v = v_{abs} - v_{em}$ of the three fluorophores vs solvent orientational polarizability, Δf , defined in Eq. 2. All Stokes shifts are relative to the value of each probe in cyclohexane, and values for the dyad and C152 are vertically displaced by 1000 and 2000 cm⁻¹ for clarity. Data in the quadrupolar solvents (toluene and dioxane) and ionic liquids are omitted from these correlations. In binary solvent mixtures, Δf is assumed to be the volume-weighted average of the values of Δf of the pure solvents.



Figure 8: Fluorescence (TCSPC) decays of the dyad in selected solvents. The uppermost curve is an H152 decay, shown for comparison. Solvents abbreviations are defined in Table 2. IRF denotes the instrument response function of the TCSPC instrument.



Figure 9: A representative KGE data set of the dyad in propylene carbonate. (a) Time-resolved spectra (solid curves) and lognormal fits (dashed). (b) The peak frequency and (c) the normalized peak height and integrated area. Symbols in panels (b) and (c) are the KGE data and the curves are multi-exponential fits.



Figure 10: Electron transfer rate constants of the dyad plotted versus emission frequency. Points denote the logarithmic average of $k_{ET}^{(1)}$ and $k_{ET}^{(2)}$, and the ends of the error bars their individual values. Electron transfer in the ionic liquids [N₈₈₈₁][Tf₂N] and [P_{14,666}][Tf₂N] is too slow to be measured, even at 353 K and the points plotted are only upper limits.

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Figure 11: TCSPC emission decays of the dyad in [Pr₄₁][Tf₂N] as a function of temperature. The inset shows the electron transfer rates derived from these decays in an Arrhenius format. The fit shown is $\ln(k_{ET}/s^{-1}) = 32.5 - 2.48(10^3 \text{ K}/T)$.

TOC Image

