

Formation of an unusual charge-transfer network from an ionic liquid†

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An intriguing and novel charge-transfer complex between dimethyldihydrophenazine and diethylviologen has been crystallized from an ionic liquid at room temperature, resulting in an interesting stacking motif of interrupted D⋯A⋯D type triads: efficient formation of the complex is seen within an ionic liquid and acetone, with the complex absorbing strongly across nearly the entire visible–NIR spectral region.

Although the initial interest in ionic liquids (ILs) arose in the areas of chemical synthesis, catalysis, and separation,¹ more recently, they have begun to emerge as solvents for applications including analytical chemistry² and non-aqueous enzymology.³ Several features including their fantastically low vapor pressures, high thermal stabilities, reasonable ionic conductivities, and broad electrochemical windows also argue their potential utility in emerging areas such as next-generation fuel cells and photovoltaic research and development.⁴ Most notable in this regard is the work of Gratzel and co-workers in which ILs were employed as electrolytes within amphiphilic polypyridyl ruthenium dye-sensitized solar cells.⁵ A number of fundamental photophysical studies on ILs ranging from dipolar solvent relaxation,⁶ preferential solvation,⁷ and translational diffusion⁸ to the elaboration of a ratiometric optical thermometer⁹ have been carried out by several of these authors and others, most notably related efforts to understand the dynamics and solvent behavior of ILs by the groups of Pagni,¹⁰ Pandey,¹¹ Samanta,¹² Gordon,¹³ Maroncelli,¹⁴ Baldelli,¹⁵ and Sarkar.¹⁶ Very recently, Wilkes *et al.* reported the use of *ab initio* calculations to design a range of novel S-containing ILs possessing non-linear optical (NLO) properties; several of the prepared ILs were indeed found to have rather large third-order susceptibilities, $\chi^{(3)}$.¹⁷ The pH-induced organization of the anionic porphyrin *meso*-tetrakis(4-sulfonatophenyl) (H_4TPPS^{2-}) into J-aggregates has also been observed within an IL.¹⁸ Beyond these reports, however, to our knowledge there have been no examples of using ILs as solvents or components in the generation of new photonic materials or devices. In particular, the effective ionic strength within ILs (*i.e.*, so-called “ionicity”) is thought to play a complex but as yet undetermined role in modulating the efficiency of electron/charge separation and transfer within ILs. And yet, very little has been done to explore electron donor–acceptor

charge-transfer (CT) pairing within these diverse fluids, to date. Here, we report an interesting CT complex crystallized from an IL, which has potential for utilization as either a new solid-state or completely fluid photomaterial at room temperature.

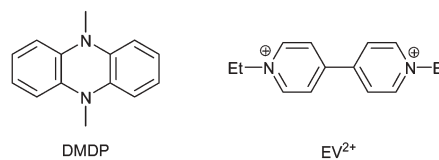
Viologens have been used extensively as electron acceptors and readily undergo outer-sphere intra- or intermolecular CT complexation with a wide range of Lewis basic donor types including halides, ferrocyanide, carboxylate anions, amines, phenols, and arenes.¹⁹ *N,N'*-Dimethyldihydrophenazine (DMDP) can likewise act either as an electron donor to form CT complexes with suitable acceptors or can reduce acceptors with large electron affinities.²⁰ In this work, crystals of the CT complex between DMDP and the electron accepting *N,N'*-diethylviologen dication (EV^{2+}) were grown from the IL *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethyl sulfonamide), $[C_4mpy][Tf_2N]$, through co-saturation of DMDP and $EV(Tf_2N)_2$ in a 1 : 1 ratio in $[C_4mpy][Tf_2N]$ at 250 °C, resulting in deep emerald-colored rod-shaped crystals.§ Rather than the infinite planar stacks typically observed in donor–acceptor CT complexes containing alternating donor–acceptor motifs of $\cdots[D\cdots A\cdots]_x\cdots$ or some variation thereof, our DMDP· EV^{2+} assembly forms infinite columns of *interrupted* stacks, in which discrete triads of $[D\cdots A\cdots D]$ are punctuated by an orthogonal EV spacer ($D = DMDP$, $A = EV^{2+}$); see Fig. 1.† The shortest interaction between DMDP and EV is 3.128 Å, which occurs between the nitrogen atoms of a DMDP molecule and the aryl carbon atoms of the planar EV^{2+} molecules sandwiching it, while the shortest carbon–carbon (C–C) distance (3.160 Å) is between aryl groups of the donor and acceptor. As a neutral species, DMDP is a bent molecule (“butterfly” geometry) which allows for the strongly donating nitrogens of two DMDP molecules to interact with a single EV^{2+} bridging molecule. This nonplanarity (DMDP flattens upon oxidation to the radical cation and dication forms) also prevents strong π – π interactions with the concave face of the DMDP. However, a convenient pocket is formed between two DMDP molecules which provides sites for edge-on (T-shaped) π interactions with the orthogonal EV^{2+} molecule. The distances between the EV^{2+} hydrogens which interact with the aryl DMDP carbons range from 2.7 to 2.9 Å and C–C intermolecular distances fall in the 3.4–3.5 Å range, typical

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Scheme 1 Structures of *N,N'*-dimethyldihydrophenazine (DMDP) and *N,N'*-diethylviologen, (EV^{2+}).

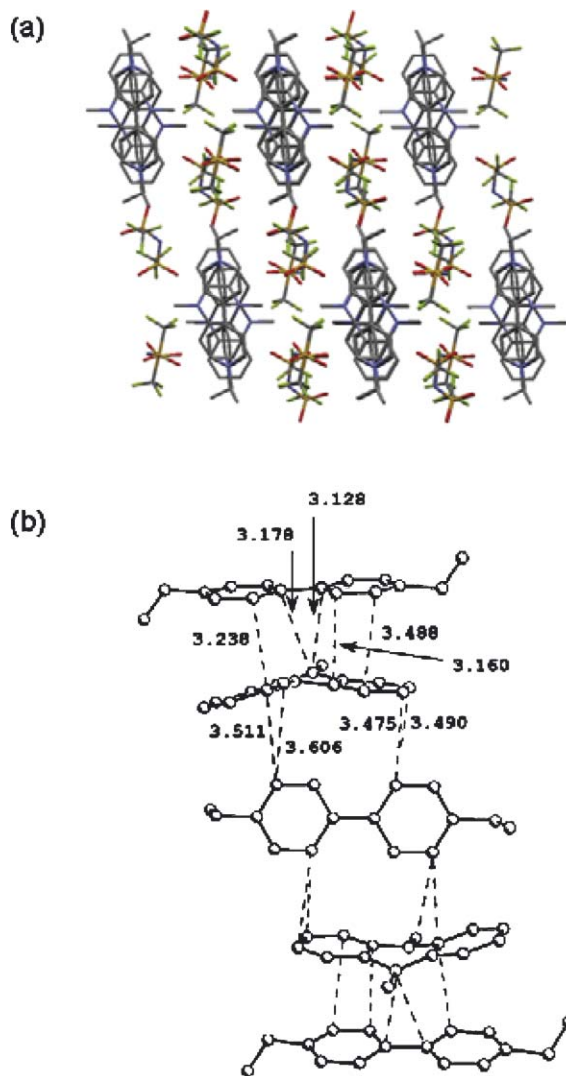


Fig. 1 (a) View down interrupted stacks of DMDP·EV²⁺, with Tf₂N⁻ anions located at inter-columnar interstices. (b) Stacking motif with shortest distances provided; a center of inversion lies at the center of the orthogonal EV molecule. Hydrogen atoms have been omitted for clarity.

for these types of edge-on π stacking interactions.²¹ This orthogonal EV²⁺ molecule is also closely packed *via* electrostatic interactions with Tf₂N⁻ anions which fill in the gaps to either side of the channel.

Plot c of Fig. 2 shows a solid-state UV-vis spectrum of a crystalline DMDP·EV²⁺ film deposited on quartz. The complex is strongly colored and exhibits a broad CT absorption above 500 nm which persists well into the near-infrared (NIR) region. In solution, while both DMDP and EV²⁺ are colorless to the eye, upon mixing the two in [C₄mpy][Tf₂N] or in acetone, a similarly broad CT band forms, with a maximum centered near 740 nm. Again, the band covers nearly the entire visible spectrum and well into the NIR, completely spanning the 500 to 1100 nm spectral window. Additions of EV²⁺ to a solution of DMDP in [C₄mpy][Tf₂N] manifest in monotonic increases in the CT absorption band. Using Job's method of continuous variation, we confirmed a 1 : 1 stoichiometry for CT complex formation within solution. An apparent association constant (K_{eq}) of $18.2 \pm 1.9 \text{ M}^{-1}$ was

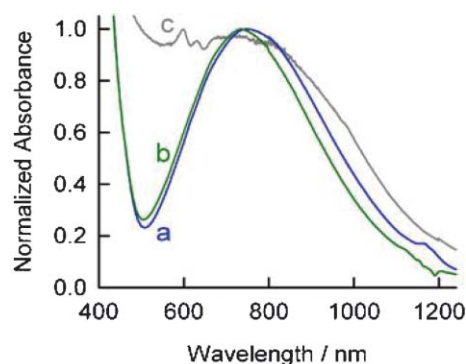


Fig. 2 Overlaid, normalized UV-vis spectra for DMDP·EV²⁺ in (a) [C₄mpy][Tf₂N], (b) acetone, and (c) as a solid thin film on quartz.

estimated on the basis of Benesi–Hildebrand analysis using the following expression²²

$$\frac{1}{A} = \frac{1}{K_{\text{eq}}\epsilon[\text{DMDP}]_0[\text{EV}^{2+}]} + \frac{1}{\epsilon[\text{DMDP}]_0} \quad (1)$$

where A is the absorbance of the CT complex at 740 nm, ϵ is the molar extinction coefficient at the same wavelength, and $[\text{DMDP}]_0$ is the initial analytical concentration of DMDP. Note that the constraint that $[\text{EV}^{2+}] \gg [\text{DMDP}\cdot\text{EV}^{2+}]$ from which eqn (1) was derived is well met within the $[\text{EV}^{2+}]$ limits used in Fig. 3b while also remaining within the confines of Beer–Lambert linearity. Titrations of the DMDP with EV²⁺ in acetone suggest similar 1 : 1 complex formation, but with a much weaker association ($K_{\text{eq}} = 3.9 \pm 0.6 \text{ M}^{-1}$). The stability of the DMDP·EV²⁺ CT complex in acetone is, as expected, of the same

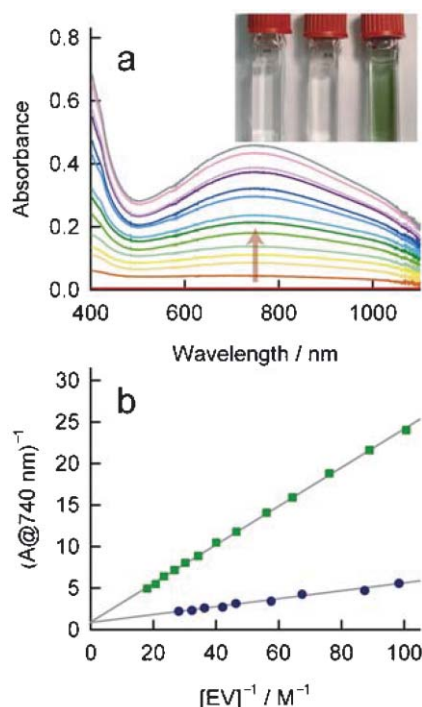


Fig. 3 (a) UV-vis spectral changes observed during DMDP·EV²⁺ CT complex formation in [C₄mpy][Tf₂N]. The arrow denotes the direction of increasing $[\text{EV}^{2+}]$ from 0 to 35.6 mM for $[\text{DMDP}]_0 = 4.7 \text{ mM}$. (b) Benesi–Hildebrand double-reciprocal plots of DMDP·EV²⁺ CT complexation in acetone (■) and [C₄mpy][Tf₂N] (●).

order of magnitude but lower than that observed for ethylamine (EA) complexation with methyl viologen (MV^{2+}) in water.²³ Quite interestingly, however, the strength of CT association is anomalously high in $[C_4mpy][Tf_2N]$, nearly 5-fold higher than in acetone. Graphical analysis ($r \geq 0.990$) also yields ϵ values at 740 nm of 273 and 246 $dm^3 mol^{-1} cm^{-1}$ in acetone and $[C_4mpy][Tf_2N]$, respectively. The latter is particularly surprising given reports that the absorptivity for CT complexes decreases markedly with the addition of inert electrolyte.^{24,25} The reported ϵ value for EA· MV^{2+} is 187 $dm^3 mol^{-1} cm^{-1}$.^{23,24} Clearly, despite the “ionicity” of ILs they do not behave in this context as simple electrolytes. The bandwidth at half-maximum is marginally higher in $[C_4mpy][Tf_2N]$ compared with acetone (6790 *versus* 6640 cm^{-1}), possibly ascribable to increased molecular motion.²³ This also accords with the 15 nm offset in the electronic absorption peak maxima which can be explained by variation of the extent of average HOMO–LUMO overlap. Again, despite growth from a 1 : 1 stoichiometric solution and indeed striking spectral similarity, the stacking observed in the solid-state exhibits a 2 : 1 complexation of DMDP with EV^{2+} . This arrangement most probably results from a crystal packing preference forced by the bent nature of DMDP within the rigid crystal.

Cyclic voltammetry of the complex in $[C_4mpy][Tf_2N]$ shows little change in the reduction potentials for the EV^{2+} when dissolved in a 1 : 1 solution with DMDP. The half-wave potentials for EV^{2+} reduction in the CT complex occur at $E_{1/2}^{2+/1+} = -0.84$ V and $E_{1/2}^{1+/0} = -1.28$ V relative to the ferrocene/ferrocenium (Fc/Fc⁺) couple. Thus, $E_{1/2}$ for the $EV^{1+/0}$ couple shifts to become more positive by 70 mV upon complexation with DMDP in the IL. DMDP oxidations in the DMDP·EV complex appear at $E_{1/2}^{1+/0} = -0.25$ V and $E_{1/2}^{2+/1+} = +0.47$ V. The DMDP is therefore not a sufficient reductant toward EV^{2+} for full electron transfer to occur, which is consistent with the lack of evidence for the blue-colored, nearly planar EV^{+} radical cation in the electronic absorbance spectra. In any case, the redox signals remain stable after continuous cycling for at least 10^5 cycles.

In summary, a complex of DMDP· EV^{2+} , formed and grown from the IL $[C_4mpy][Tf_2N]$, results in a unique crystal stacking arrangement in which interrupted CT arrays of discrete $[D \cdots A \cdots D]$ trimers are separated by an orthogonally-rotated EV^{2+} unit which interacts with DMDP neighbors *via* edge-on π interactions. The CT complex is evident in solution as well as the solid-state, however a 1 : 1 complex is observed in the former whereas a 2 : 1 stacking exists in the latter. We anticipate that the number of potential uses will grow for similarly-derived materials including display, memory, chemical sensing, optoelectronic, optical limiting, and light modulation/shutter applications.

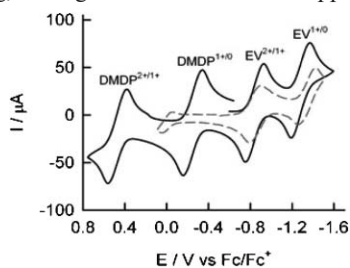


Fig. 4 Cyclic voltammograms of $EV(Tf_2N)_2$ (dashed line) and a 1 : 1 solution of DMDP : EV^{2+} (solid line), both in $[C_4mpy][Tf_2N]$ (scan rate = $100 mV s^{-1}$; Pt disk working electrode; Ag/AgCl pseudo-reference electrode).

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Notes and references

§ Crystal data for DMDP· EV^{2+} : $C_{32}H_{32}F_{12}N_6O_8S_4$, $M = 984.88$, $a = 12.490(5)$, $b = 12.820(5)$, $c = 13.993(6)$ Å, $\alpha = 71.643(6)^\circ$, $\beta = 72.240(7)^\circ$, $\gamma = 82.390(8)^\circ$, $V = 2023(1)$ Å³, triclinic space group $P\bar{1}$, $Z = 2$, $T = 203$ K, $R1(I > 2\sigma) = 0.0607$, and $wR2(I > 2\sigma) = 0.1568$. The reflection data were collected on a Bruker P4/CCD using ϕ scans. The structure was solved using standard direct methods techniques (SHELXS-97),²⁶ and refined using full-matrix least-squares based on F^2 (SHELXL-97).²⁶ Hydrogen atom positions were idealized, and rode on the atom they were attached to. All non-hydrogen atoms were refined anisotropically. CCDC 284569. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513893k

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