

## The Degree of Charge Transfer in Ground and Charge-Separated States Revealed by Ultrafast Visible Pump/Mid-IR Probe Spectroscopy

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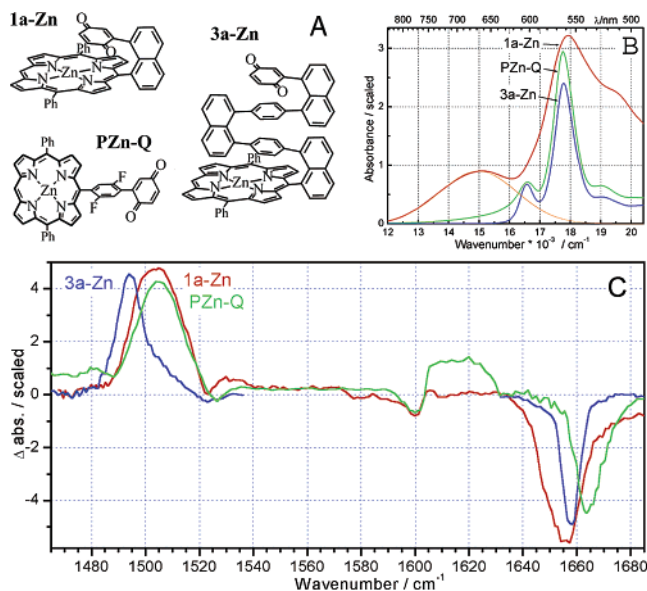
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An open challenge in charge-transfer (CT) chemistry is to quantify the degree of ground-state CT in weakly interacting donor–acceptor systems. While various absorption and scattering techniques provide information about CT,<sup>1–6</sup> they tend to be less reliable for weakly coupled systems. This report describes a new femtosecond visible pump/mid-IR probe spectroscopic approach to assess directly the ground- and excited-state degrees of CT in donor–spacer–acceptor (D–Sp–A) structures.

Two classes of (porphyrinato)zinc(II) (PZn)-based D–Sp–A compounds with either quinonyl (Q) (**1a-Zn**, **3a-Zn**, **PZn-Q**;<sup>7</sup> Figure 1A) or *N*-(*N'*-octyl)pyromellitic diimide (PI) (**PZn-PI**, **PZn(PI)**;<sup>8,9</sup> Figure 2B) electron acceptors were interrogated. These molecules have a range of Sp structures and exploit conventional linear and  $\pi$ -stacked coupling motifs. Carbonyl antisymmetric stretching mode frequency domain transient-IR spectra of these species were recorded and analyzed for the Q/PI moieties. The characteristic A modes shift to significantly lower energy relative to the ground-state frequencies in the respective charge-separated (CS) states of these complexes (Table 1, Figure 1). The frequency shifts reflect the decreased force constants for these modes in the CS state, tracking the augmented A-localized electronic charge in this staterelative to the ground state.

Interestingly, the magnitude of the carbonyl frequency shift between the ground and CS state,  $\Delta\nu_A$ , varies in compounds featuring the same acceptor moiety (Table 1). For example,  $\Delta\nu_A$  is  $\sim 7.3\%$  smaller in **1a-Zn** as compared to that observed in **3a-Zn** (Table 1). Note also that the **1a-Zn** ground-state frequency ( $\nu_A$ ) is red-shifted while its corresponding CS-state frequency ( $\nu_A^-$ ) is blue-shifted with respect to the analogous modes of **3a-Zn**.

As the D and A moieties in **1a-Zn** are juxtaposed, there is substantial mixing of the neutral (D–Sp–A,  $\psi_0$ ) and charge-resonance ( $D^+Sp-A^-$ ,  $\psi_1$ ) wave functions in the ground state ( $\psi_G$ ),<sup>1,2</sup> signified by a pronounced CT band (Figure 1B). The properties of the ground and CS states can be described by the admixtures of the  $\psi_0$  and  $\psi_1$  wave functions.<sup>1,2</sup> The contribution of the charge-resonance wave function,  $\psi_1$ , in the ground electronic state can be estimated from the electronic coupling matrix element  $H_{DA}$ ,<sup>10</sup>  $C_2 \approx |H_{DA}/\Delta E|$ , where  $\Delta E$  is the ground-to-CS state energy gap. The magnitude of the ground-state dipole moment, as well as the degree to which charge is localized on A in the ground state, scales with  $C_2^2$ . The Q/PI carbonyl mode acceptor frequency depends on the vibrational force constant ( $k$ ),  $\nu_{CO} = \sqrt{k/m}/2\pi c$ . The force constant in the ground and CS states changes with a weighted average contribution of the charge resonant state. If the frequency change,  $\Delta\nu_A$ , is small relative to the ground-state frequency ( $\Delta\nu_A \ll \nu_A$ ;  $\Delta\nu_A = \nu_A - \nu_A^-$ ) and the D–A interaction is weak ( $\delta \ll \Delta\nu_A$ , where  $\delta$  is the frequency change in the ground state due to the contribution of the charge-resonance state), the magnitude of  $\delta$  can be computed from



**Figure 1.** Structures of the quinonyl-based D–Sp–A complexes (A); linear visible spectra (B), and transient IR spectra (C) of **1a-Zn**, **3a-Zn**, and **PZn-Q**. Time delays for the **1a-Zn**, **3a-Zn**, and **PZn-Q** transient spectra are, respectively, 0.6, 5.0, and 1.7 ps (experimental conditions:  $\lambda_{ex} = 580$  nm, solvent = 99:1  $CDCl_3$ :pyridine-*d*<sub>5</sub>,  $T = 23$  °C).

the value of  $C_2^{2,1} \delta \approx \Delta\nu_A^\circ C_2^2$ , where  $\Delta\nu_A^\circ = \nu_A^\circ - \nu_A^{-\circ}$ , and  $\nu_A^\circ$  and  $\nu_A^{-\circ}$  are ground- and CS-state Q/PI vibrational frequencies that lack contributions, respectively, from the  $\psi_1$  and  $\psi_0$  wave functions. The experimentally measured relative frequency shift  $\xi$  ( $\xi = (\Delta\nu_A^\circ - \Delta\nu_A)/\Delta\nu_A^\circ$ ) can be used to estimate the extent to which the CT wave function contributes to  $\psi_G$ ; this approach has been employed previously in transient Raman analysis of MLCT states.<sup>6c</sup> Since  $\xi \approx 2C_2^2$ ,  $C_2^2$  is expected to scale with the Mulliken population on the acceptor ( $P_Q$ ).<sup>11</sup>

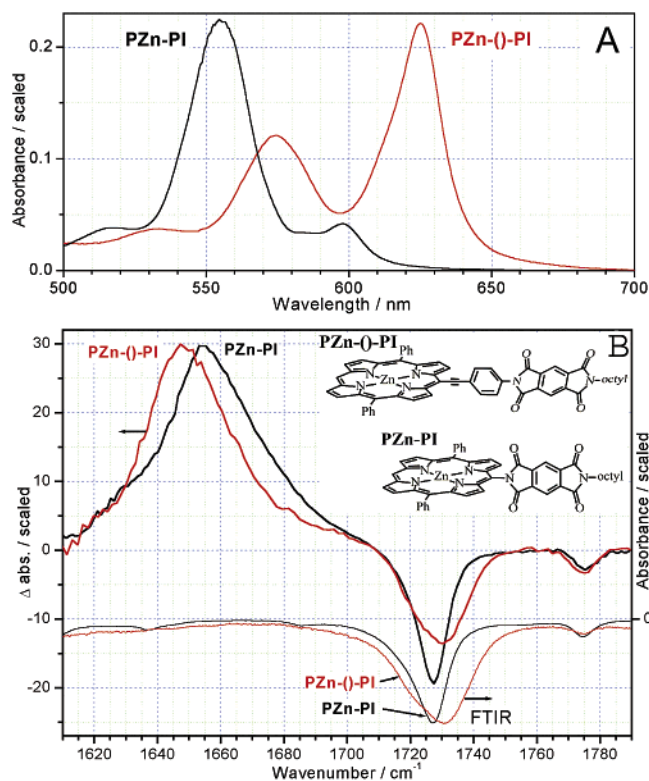
In **3a-Zn**, the D-to-A centroid distance is  $\sim 10.5$  Å.<sup>7</sup> We therefore assume that  $\psi_1$  contributes little to  $\psi_G$ , and approximately one unit of charge is transferred from D to A in the CS state, and we take the measured **3a-Zn**  $\nu_A$  and  $\nu_A^-$  frequencies to be reasonable approximations for  $\nu_A^\circ$  and  $\nu_A^{-\circ}$ , respectively. In **1a-Zn**, the minimum D–A interplanar separation (2.97 Å) is less than the van der Waals contact distance.<sup>7</sup> As such, strong mixing of  $\psi_0$  and  $\psi_1$  wave functions is anticipated. This mixing should serve to enhance ground-state polarization and, correspondingly, diminish CS state polarization in **1a-Zn** with respect to that observed in the analogous states of **3a-Zn**.

The experimentally determined charge-resonance contribution to the ground state ( $\xi/2$ ) of **1a-Zn** is 3.7%. A smaller contribution (1.5%) was determined for **PZn-Q**, where a difluorophenyl bridge connects the porphyrin-5 and quinonyl-2 positions (Figure 1C, Table 1).

The charge-resonance contribution ( $C_2^2$ ) to  $\psi_G$  can also be

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**Figure 2.** (A) **PZn-PI** and **PZn(O)PI** linear visible spectra. (B) Transient IR spectra and linear FTIR spectra obtained for **PZn-PI** and **PZn(O)PI**. The time delays for the transient spectra are, respectively, 0.5 and 0.87 ps (experimental conditions:  $\lambda_{\text{ex}}(\text{PZn-PI}) = 595$  nm;  $\lambda_{\text{ex}}(\text{PZn(O)PI}) = 620$  nm; solvent = 99:1  $\text{CDCl}_3$ :pyridine-*d*<sub>5</sub>,  $T = 23$  °C).

**Table 1.** Ground ( $\nu_A$ )- and CS ( $\nu_A^-$ )-State Acceptor Frequencies, along with Absolute ( $\Delta\nu_A$ ) and Relative ( $\xi$ ) Frequency Differences and Ground-State Acceptor Population ( $2P_0$ )

	$\nu/\text{cm}^{-1}$	$\nu_A^-/\text{cm}^{-1}$	$\Delta\nu/\text{cm}^{-1}$	$\xi, \%$	$2P_0, \%$
<b>3a-Zn</b>	1658.0	1494.3	163.7	0 <sup>a</sup>	
<b>1a-Zn</b>	1655.7	1503.9	152	7.3 ± 0.7	7.4
<b>PZn-Q</b>	1664	1505	159	2.9 ± 0.6	0.9
<b>PZn(O)PI</b>	1730.3	1647.5	82.8	0 <sup>a</sup>	
<b>PZn-PI</b>	1727.4	1654.5	72.9	12 ± 1.2	5.7

<sup>a</sup> Assumes that one full unit of charge is transferred within the initially prepared CS state. <sup>b</sup>  $P_0$  is the computed Mulliken population on A expressed as the percentage of an electron charge based on analysis of the quasi-degenerate porphyrin frontier orbitals averaged over thermally accessible geometries.

estimated from the electronic coupling matrix element ( $H_{DA}$ ). Independent estimation of the electronic coupling matrix element ( $H_{DA}$ ) can be made via classic analysis of the intensity of the CT transition,<sup>3</sup>  $H_{DA} = 2.06 \times 10^{-2} \sqrt{\nu_{\text{max}} \epsilon_{\text{max}} \Delta\nu_{\text{fwhm}}}/R_{DA}$ . Here  $\nu_{\text{max}}$ ,  $\Delta\nu_{\text{fwhm}}$ , and  $\epsilon_{\text{max}}$  are the peak frequency, bandwidth, and peak extinction coefficient, respectively, and  $R_{DA}$  is the D-to-A center-to-center distance. A pronounced CT band can be seen for **1a-Zn** (Figure 1B),<sup>12</sup> with  $\nu_{\text{max}} = 14\,980$   $\text{cm}^{-1}$ ,  $\Delta\nu_{\text{fwhm}} = 2\,980$   $\text{cm}^{-1}$ , and  $\epsilon_{\text{max}} = 2.6 \times 10^3$   $\text{cm}^{-1} \text{M}^{-1}$ , giving  $H_{DA} = 2\,330$   $\text{cm}^{-1}$ . Using  $\Delta E \approx 13\,000$   $\text{cm}^{-1}$ , a  $C_2^2$  value of 0.032 is obtained, which is remarkably close to the  $\xi/2$  value (0.037) calculated from the IR band shifts (Table 1).

Similar data that chronicle frequency shifts for D-Sp-A compounds with **PI** acceptors are shown in Figure 2 and Table 1;  $\nu(\text{PI}^-) - \nu(\text{PI})$  for **PZn-PI** is  $\sim 12\%$  smaller than that observed for **PZn(O)PI** (Figure 2B, Table 1). The enhanced ground- and diminished CS-state polarization in **PZn-PI** relative to **PZn(O)PI** reflect the single-bond D–A separation in **PZn-PI** and the fact that substantial Coulombic interactions stabilize its CS state.<sup>9</sup> The  $\psi_1$  wave function contribution to  $\psi_G$  is much larger in **PZn-PI** as compared to that in **PZn(O)PI**, despite the near orthogonal orientation of D and A

moieties in **PZn-PI**.<sup>8,13</sup> This conclusion is consistent with previously published data that indicate  $\psi_G$  for **PZn(O)PI** possesses little amplitude on the intervening ethynyl group,<sup>9</sup> that electronically isolated PZn and PI units. The Figure 2 transient data also underscore a dramatic increase of the **PI**<sup>-</sup> bandwidth in the **PZn-PI** CS state relative to that observed for the ground-state **PI**<sup>0</sup> absorbance, signaling augmented CS-state structural inhomogeneity. Given the **PZn-PI** structure, this inhomogeneity is largely reflected in the PZn-to-PI torsional angle distribution.<sup>13</sup> The magnitude of the **PI**<sup>-</sup>/**PI**<sup>0</sup> frequency shifts is half as large as the analogous **Q**<sup>-</sup>/**Q**<sup>0</sup> shifts in these D-Sp-A systems, highlighting a clear correlation of  $\Delta\nu_A$  with A size and the sensitivity of the force constants to A charge density.

The experimentally determined degrees of charge transfer are mirrored in semiempirical (ZINDO) ground-state calculations on the structures (Table 1). The analysis indicates qualitative agreement between computed ground-state charge transfer and that determined by the pump/mid-IR probe spectroscopy.

In conclusion, we have demonstrated a new, useful approach to determine the extent of CT in ground and CS states using visible pump/mid-IR probe spectroscopy. These data show that the frequency shift,  $\Delta\nu_A$ , established by this method provides a more accurate measure of the degree of CT as compared to the methods<sup>5,6</sup> which rely on the ground-state frequency shift alone, as determination of  $\Delta\nu_A$  largely factors out frequency shifts that derive from the local electrostatic environment. This added accuracy, coupled with the ability of this method to interrogate the electronic interaction matrix element between ground and CS states, enable determination of new experimental benchmarks to test the power of complimentary computational methods. Further, we note that this approach may find particular utility when CT transitions either overlap strongly with other bands or possess low oscillator strength.

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- (10) The assumptions made include orthogonality of the  $\psi_0$  and  $\psi_1$  wave functions and a weak interaction limit approximation.
- (11) Mulliken population analysis:  $q_A = Z_A - \sum_{\mu \in A} (\mathbf{P}\mathbf{S})_{\mu\mu}$ , where  $Z_A$  is the charge of atomic nucleus A,  $\mathbf{P}$  is the density matrix, and  $\mathbf{S}$  is the overlap matrix; the index of summation indicates that we only sum over the basis functions centered on A.
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