

# Infrared spectroscopic determination of the degree of charge transfer in complexes of TCNE with methyl-substituted benzenes†

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**The position of the CN stretching frequency in infrared spectra of tetracyanoethylene (TCNE) complexed with methyl-substituted benzenes is used to determine the fraction of charge transferred from the electron donor to the acceptor.**

Interest in charge transfer (CT) complexes between tetracyanoethylene (TCNE) and aromatic electron donors has recently been renewed, as prospective molecular electronic devices are being investigated.<sup>1,2</sup> A self-assembled monolayer (SAM) of the CT complex formed by TCNE and the dithiol analogue of hexamethylbenzene (HMB), tetramethylxylyldithiol (TMXYL) on Au(111) has recently been investigated in a molecular electronics study.<sup>1</sup> The CT complex was shown to be nearly one hundred times more conducting when compared to a SAM of TMXYL alone on Au(111). Also, electrostatic force microscopy has been used to evaluate the surface potentials of SAMs of TMXYL and TMXYL-TCNE on Au(111).<sup>2</sup> CT complexes hold promise as useful conducting structures in molecular electronics.

Investigators since the 1950's have been interested in CT complexes like tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) and HMB-TCNE and their analogues because of their interesting spectroscopic properties,<sup>3</sup> including time-resolved Raman spectroscopy,<sup>4-6</sup> and for their potential use as molecular metals.<sup>7</sup> For example, Miller and coworkers have done extensive work on ferromagnetic TCNE salts<sup>8-11</sup> while others have investigated conductive properties of TCNE and TCNQ compounds.<sup>12-14</sup> One problem with conduction in crystals of these molecular metals is that Peierls distortions tend to localize charge and inhibit the ability of the CT complex crystals to conduct.<sup>15</sup> Reducing the size of conducting CT complex structures to the nanoscale (by using single molecules rather than extended crystals) is one way to eliminate Peierls distortions. Another potentially useful feature of CT complexes is the ability to synthetically tune their electronic properties by suitable modification of the donor or acceptor molecules. The conducting capabilities of CT complexes are optimal when an electron is equally shared by the donor (D) and the acceptor (A).<sup>16</sup> In this communication, we describe the relationship between the CN stretching frequency,  $\nu_{\text{CN}}$ , of TCNE in CT complexes with aromatic donors and the ionization potential,  $I_{\text{p}}$ , of the donor molecules. We report a spectroscopic method to estimate the degree of charge transfer between TCNE

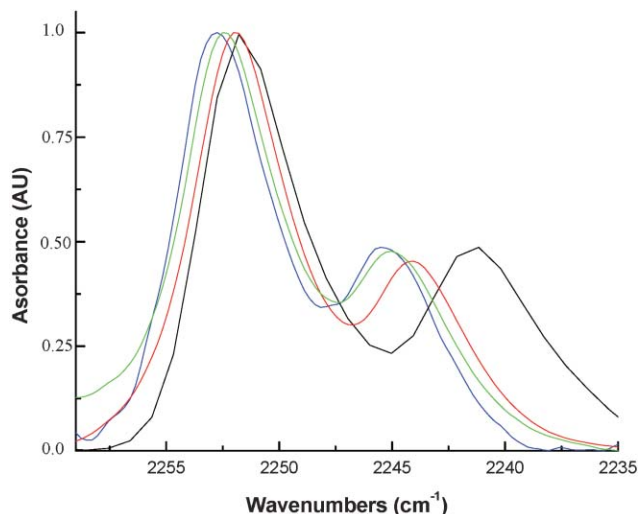
and methyl-substituted donors by comparing  $\nu_{\text{CN}}$  of the complex to  $\nu_{\text{CN}}$  of free TCNE, its radical anion, and dianion.

Tetracyanoethylene (TCNE), purchased from Aldrich, was purified by either sublimation or by dissolving TCNE in dichloromethane, filtering, evaporating the solvent from the filtrate and recrystallizing at  $-40$  °C in a minimal amount of a 1 : 1 solution of dichloromethane and acetonitrile. All electron donors were purchased from Aldrich and used without further purification.

Charge transfer complexes of electron acceptor tetracyanoethylene (TCNE) with methyl-substituted benzene electron donors were prepared for infrared spectroscopic analysis using one of two methods depending on the phase of the electron donor. For the solid aromatic donors, hexamethylbenzene (HMB) and pentamethylbenzene (PMB), 1 equivalent of TCNE and 1.2 equivalents of the donor were dissolved in a minimal amount of dichloromethane and the solvent was allowed to evaporate, leaving deeply colored crystals. These crystals were pressed into KBr pellets and IR spectra were taken. For the liquid aromatic donors, benzene (BEN), toluene (TOL), xylenes (mixture of *ortho*-, *para*-, and *meta*-, XYL), and mesitylene (1,3,5-trimethylbenzene, MES), 15 mM TCNE solutions were prepared in the donor solvent and IR spectra were taken in a liquid IR cell. The liquid IR samples were run against a background of the donor solvent. Although some regions of the spectra were obscured by poor background subtraction of the IR active solvents, the CN stretching region ( $\sim 2250$   $\text{cm}^{-1}$ ) was clearly visible. There was no apparent difference in the CN stretching region for spectra taken using the preparations above or for spectra taken in dichloromethane solutions, provided the appropriate ratio of concentration for the donor to TCNE is chosen (e.g. 20 : 1 for HMB-TCNE).

Infrared spectra of the charge transfer complexes were taken with a resolution of  $0.5$   $\text{cm}^{-1}$  and 64 scans using a Bruker Equinox 55 spectrometer. The  $\nu_{\text{CN}}$  spectrum for free TCNE shows two peaks at  $2259$   $\text{cm}^{-1}$  and  $2218$   $\text{cm}^{-1}$ . Fig. 1 shows the IR spectra of CT complexes of TCNE with arene donors above  $2235$   $\text{cm}^{-1}$ . The lower energy shoulder observed in the CT complexes is well known to shift due to the presence of structurally different CT complex conformers with regard to the relative position of TCNE above the aromatic ring.<sup>17,18</sup> Since the lower energy shoulders are complicated by the presence of conformers, rather than by the changes in electron density of TCNE alone, only the peak positions of the high energy peaks of each spectrum shown in Fig. 1 will be discussed. The high energy  $\nu_{\text{CN}}$  mode involves net CN displacements parallel to, and the low energy mode transverse to the C=C double bond. Since the C=C bond order is reduced upon introduction of electron density to TCNE, it is to be expected that

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**Fig. 1** CN stretching region of infrared spectra of CT complexes of TCNE with benzene (blue), toluene (green), mesitylene (red) and hexamethylbenzene (black). Peak intensities are normalized.

the high frequency mode is more sensitive to charge. DFT normal mode calculations fully justify comparing the high frequency mode of TCNE<sup>0</sup> to the one of TCNE<sup>1-</sup>. The high frequency bands shown in the spectra in Fig. 1 correspond to the  $b_{2u}$   $\nu_{(\text{CN})}$  mode of free TCNE where it appears at 2259 cm<sup>-1</sup> (not shown). This frequency is reduced to 2253 cm<sup>-1</sup> for the TCNE–benzene complex. As the degree of methyl substitution (and, therefore, the electron density of the donor  $\pi$  system) increases, the mode monotonically shifts to lower energy. The donation of electron density to the LUMO of TCNE puts electron density into the antibonding  $\pi^*$  orbitals of the C≡N moieties, lowering the value of the spring constant,  $k$ , and causing the shift to lower energy. The relationship between the electronic structure and the spring constant is expressed using Mulliken theory in terms of the overlap integral,  $S_{01}$ , in eqn. (1).<sup>19,20</sup>

$$\frac{(k_0 - k_N)}{k_0} = \frac{\Delta k}{k} = 1 - \frac{k_1}{k_0} (b^2 + abS_{01}) \quad (1)$$

where  $k_0$  and  $k_1$  are the  $\nu_{(\text{CN})}$  force constants in free TCNE and TCNE<sup>-1</sup> respectively,  $k_N$  is the force constant for the CN bond in the CT complex, and  $a$  and  $b$  are the coefficients of the “no bond” and “dative” functions in the ground state wave function of the complex. Coefficients  $a$  and  $b$  are defined in the relationship in eqn. (2),

$$\psi_{\text{N}}(\text{DA}) = a\psi_0(\text{D,A}) + b\psi_1(\text{D}^+ - \text{A}^-) \quad (2)$$

where  $\psi_{\text{N}}(\text{DA})$  is the total wavefunction of the complex between D and A,  $\psi_0(\text{D,A})$  is the “no bond” wavefunction, and  $\psi_1(\text{D}^+ - \text{A}^-)$  is the “dative” wavefunction. For weakly bound CT complexes, like those reported here, the coefficient of the dative function,  $b$ , is equivalent to the amount of charge transferred from D to A.<sup>19</sup> The value of  $b$  is determined from eqn. (1) by making the assumption that for weakly bound CT complexes the overlap integral,  $S_{01}$ , is zero.<sup>19</sup>

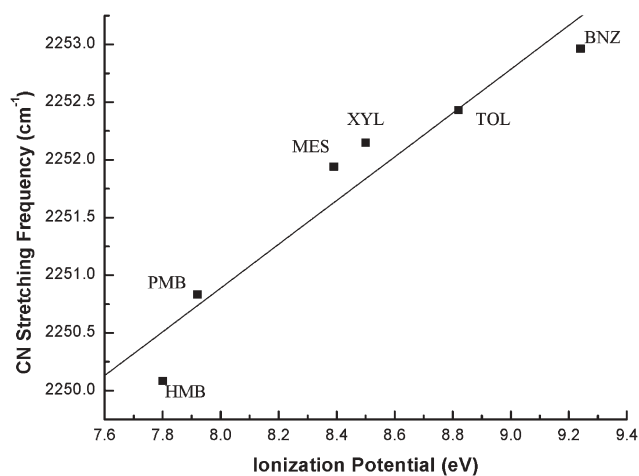
Linear correlations between the oxidation potentials and  $I_{\text{P}}$  for  $\pi$  complexes of arene donors with metals have been made.<sup>21</sup> Early

reports of spectroscopic properties of CT complexes included linear plots of the energy of the CT band,  $E_{\text{CT}}$ , vs.  $I_{\text{P}}$ .<sup>3,20</sup> Chappell *et al.* reported a linear plot of  $\nu_{(\text{CN})}$  of TCNQ salts vs. the degree of charge transfer,  $Z$ , for known complexes and determined  $Z$  based on  $\nu_{(\text{CN})}$ .<sup>22</sup> Here, we report a linear relationship between  $\nu_{(\text{CN})}$  and  $I_{\text{P}}$  of the methyl-substituted arene electron donors. Thus, the ability of an electron donor to donate electron density can be quantitatively assessed by examining the ionization potential for the electron donors. Fig. 2 shows a plot of the CN stretching frequency of the CT complexes of arene donor–TCNE complexes vs. the vertical ionization potentials<sup>21</sup> of the methyl-substituted electron donors, BEN, TOL, XYL, MES, PMB, and HMB. The linear relationship has a slope of 1.90 cm<sup>-1</sup>/eV with an  $R^2$  value of 0.920, and serves as a reasonable scale for predicting the frequency of an unknown CT complex based on the  $I_{\text{P}}$  of the electron donor.

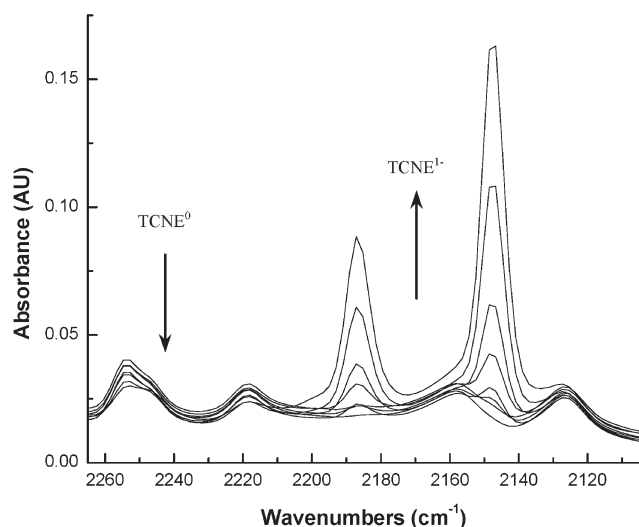
Time-resolved resonance Raman spectroscopy and picosecond infrared spectroscopy have been used to probe MLCT excited states.<sup>23–25</sup> In this study, the degree of charge transferred to TCNE by an electron donor,  $\nu_{(\text{CN})}$  for a given CT complex is compared to  $\nu_{(\text{CN})}$  of TCNE<sup>0</sup>, TCNE<sup>1-</sup>, and TCNE<sup>2-</sup>. The  $\nu_{(\text{CN})}$  modes of the TCNE<sup>0</sup> and TCNE<sup>1-</sup> (Fig. 3) are similar to those observed for the CT complexes but lack the lower energy shoulders due to conformers discussed above. The spectra of TCNE<sup>0</sup>, TCNE<sup>1-</sup>, and TCNE<sup>2-</sup> were taken in a custom-built spectroelectrochemistry cell described elsewhere.<sup>26</sup> The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in methylene chloride. Under bulk electrolysis conditions, TCNE<sup>0</sup> is reduced to TCNE<sup>1-</sup> without observing any intermediately charged species, and then to TCNE<sup>2-</sup>.

The peaks for  $\nu_{(\text{CN})}$  of TCNE<sup>0</sup> appear at 2259 cm<sup>-1</sup> ( $b_{2u}$ ) and 2218 cm<sup>-1</sup> ( $b_{3u}$ ), while the peaks for  $\nu_{(\text{CN})}$  of TCNE<sup>1-</sup> appear at 2187 cm<sup>-1</sup> and 2147 cm<sup>-1</sup>. The peaks for TCNE<sup>2-</sup> (not shown) appear at 2128 cm<sup>-1</sup> and 2073 cm<sup>-1</sup>. The peaks for TCNE<sup>1-</sup> and TCNE<sup>2-</sup> are more intense due to the increase in magnitude of the electronic dipole moment upon reduction of the TCNE. Comparison of the highest energy peaks of  $\nu_{(\text{CN})}$  for TCNE<sup>0</sup>, TCNE<sup>1-</sup>, and TCNE<sup>2-</sup> give the relationship described in eqn. (3),

$$\nu_{(\text{CN})} = -66Z + 2257 \quad (3)$$



**Fig. 2** CN stretching frequency of CT complexes of TCNE with methyl-substituted benzenes vs. ionization potential for methyl-substituted benzenes.



**Fig. 3** Spectroelectrochemical infrared spectra of TCNE upon reduction to TCNE<sup>1-</sup>.

**Table 1** CN stretching frequency and partial charge imparted to TCNE by methyl-substituted benzenes

Electron donor	$\nu_{\text{CN}}/\text{cm}^{-1}$	$Z^a$	$b^b$
Benzene	2252.9	0.060	0.075
Toluene	2252.4	0.070	0.080
Xylenes	2252.1	0.075	0.080
Mesitylene	2251.9	0.080	0.080
Pentamethylbenzene	2250.8	0.095	0.085
Hexamethylbenzene	2250.0	0.10	0.090

<sup>a</sup>  $Z$  is the fraction of charge measured by the direct IR spectroscopic method. <sup>b</sup>  $b$  is the weight of the dative structure calculated from eqn. (1), assuming  $S_{01} = 0$ .

where  $Z$  is the degree of charge donated to TCNE ( $R^2 = 0.997$ ). Devlin and coworkers reported<sup>27</sup> that  $Z$  for weakly bound CT complexes between TCNE and the donors PMB and HMB is roughly 5–10%. Here, a value of  $Z$  for each CT complex is estimated using simple IR techniques and eqn. (3). These data are shown in Table 1. For comparison, the values of the weight of the dative structure,  $b$ , for each CT complex are also shown in Table 1. The values of  $Z$  and  $b$  are in agreement with the values reported by Devlin.<sup>27</sup> Although the  $b$  values are slightly smaller than  $Z$  for all CT complexes reported here, their values are in reasonable agreement given the assumptions that have been made.

The ability to estimate  $Z$  by simple and direct IR methods allows predictions to be made about the ability of a specific surface-confined CT complex to conduct in molecular electronic applications. The IR technique described here has been used to show binding of TCNE to Au(111) confined electron donors and to determine  $Z$  for such complexes. Work on tuning the

conduction of CT complexes on Au(111) and silicon surfaces by changing the donor strength is ongoing and will be reported separately.

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