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Selectivity in the Interaction of Electron Donor and Acceptor Molecules with Graphene and Single-Walled Carbon Nanotubes

Neenu Varghese,[†] Anupama Ghosh,[†,‡] Rakesh Voggu,[†] Sandeep Ghosh,[†,‡] and C. N. R. Rao*,[†,‡]

Chemistry and Physics of Materials Unit, New Chemistry Unit and CSIR Centre of Excellence in Chemistry, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P. O., Bangalore 560064, India, and Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

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Interaction of electron donor and acceptor molecules with graphene samples prepared by different methods as well as with single-walled carbon nanotubes (SWNTs) has been investigated by isothermal titration calorimetry (ITC). The ITC interaction energies of the graphene samples and SWNTs with electron acceptor molecules are higher than those with electron donor molecules. Thus, tetracyanoethylene (TCNE) shows the highest interaction energy with both graphene and SWNTs. The interaction energy with acceptor molecules varies with the electron affinity as well as with the charge-transfer transition energy for different aromatics. Metallic SWNTs interact reversibly with electron acceptor molecules, resulting in the opening of a gap.

Introduction

Recent investigations of the interaction of electron donor and acceptor molecules with single-walled carbon nanotubes (SWNTs) have shown that molecular charge transfer affects the electronic structure of the nanotubes.[1−4] Thus, by the interaction of tetracyanoethylene (TCNE) and tetrathiafulvalene (TTF), it has been possible to introduce metallic to semiconducting transition and vice versa, but specificity of interaction with respect to the electronic nature of the SWNTs is not established. Interaction of electron donor and acceptor molecules with few-layer graphene has been investigated using Raman spectroscopy and other techniques. Molecular charge-transfer interaction between these molecules and graphene causes marked changes in the electronic structure of graphene.[5] First-principles calculations based on the DFT-GGA method suggest the interaction of graphene with donor and acceptor molecules to involve charge transfer, giving rise to the associated Raman band shifts.[6] We felt that it was important to carry out a comparative investigation of the interaction of donor and acceptor molecules with graphene and SWNTs in terms of the relative interaction energies. For this purpose, we have employed isothermal titration calorimetry (ITC) to measure the heats of interaction of a few electron donor and acceptor molecules with graphene and SWNTs. ITC is known to be a sensitive tool to study such binding interactions, as illustrated in the case of nucleobases.[7,8] ITC may not provide actual interaction energies but gives trends in interaction energies. Since SWNTs prepared by arc discharge and other methods constitute mixtures of semiconducting and metallic species,[9] we have investigated the interaction of pure metallic nanotubes, specially prepared by a new method, with donor and acceptor molecules, in order to examine the specificity of interaction. Besides showing that electron-withdrawing mol-

ecules interact more strongly with graphene and SWNTs, the present study demonstrates that doping by charge transfer changes the Fermi level of SWNTs, to create a band gap in the initially metallic SWNTs. In the case of graphene also, a band gap is opened through charge transfer by electron acceptor molecules.

Experimental Section

Isothermal titration calorimetric experiments were carried out with graphene samples prepared by three different methods, namely, thermal exfoliation of graphitic oxide (EG),[10] arc discharge of graphite in hydrogen (HG),[11] and conversion of nanodiamond (DG).[12] Dodecylamide derivatives of EG (EG-A) and DG (DG-A) were prepared by the literature procedure.[13] The graphene samples were characterized by atomic force microscopy (AFM), transmission electron microscopy (TEM), field-emission scanning electron microscopy (FESEM), and Raman spectroscopy. The EG, DG, and HG samples contained 3−4, 5−6, and 2−3 layers, respectively. The surface area of the HG sample is small ($\sim$400 m^2 g^{-1}) compared to DG ($\sim$800 m^2 g^{-1}) and EG ($\sim$1100 m^2 g^{-1}). EG-A, DG-A, and HG dispersed in toluene were used in the experiments.

ITC experiments were carried out with 1 mg mL^{-1} dispersions of graphene. The graphene dispersion was taken in the sample cell of the isothermal titration calorimeter and the reference cell filled with toluene. 10 mM solutions of tetracyanoethylene (TCNE), tetracyanoquinodimethane (TCNQ), 2,4,7-trinitrofluorenone (TNF), tetrathiafulvalene (TTF), and *N,N*-dimethyl para-phenylenediamine (DMPD) were prepared in toluene. In each experiment, 10 μL of 10 mM of each of these solutions taken in a syringe was added in equal intervals of 3 min to the sample cell and the heat changes were measured after each addition. The experiments were carried out at a constant temperature of 26 °C. Control experiments were performed by titrating the respective molecules against toluene under the same conditions, and the data so obtained were subtracted from the experimental data to eliminate the dilution effect.

* To whom correspondence should be addressed. E-mail: cnrrao@jncasr.ac.in. Fax: +91 80 22082760.
[†] Jawaharlal Nehru Centre for Advanced Scientific Research.
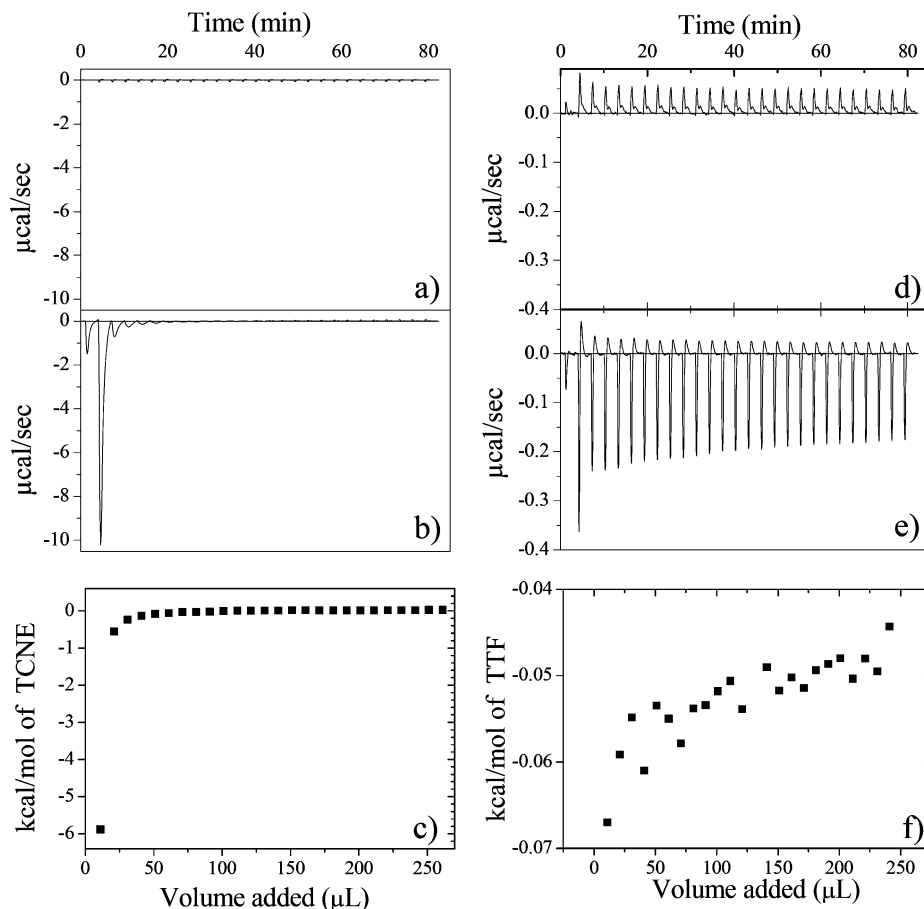[‡] Indian Institute of Science.

Figure 1. ITC data recorded for the interaction of TCNE and TTF with EG-A. ITC response for the blank titration with TCNE (a) and TTF (d). The raw ITC data for the titration of TCNE and TTF with 1.0 mg mL^{-1} of EG-A is shown in parts b and e. Parts c and f show the integrated heat of reaction at each injection of TCNE and TTF, respectively.

SWNT samples were prepared by the arc discharge method and purified by successive acid and hydrogen treatment.[14,15] Metallic SWNTs were prepared by DC arc evaporation of a graphite rod containing the Ni+Y$_2$O$_3$ catalyst, under a continuous flow of helium bubbled through Fe(CO)$_5$.[16] The samples so obtained were nearly pure metallic SWNTs (around 95%). SWNT samples dispersed in *o*-dichlorobenzene (DCB) were sonicated for 1 h to obtain 1 mg mL^{-1} solutions. Interaction of SWNTs with donor and acceptor molecules was studied in DCB solvent in the same manner as the graphene samples. In order to compare the results obtained with graphene and SWNTs, graphene samples (EG, EG-A, and HG) were also dispersed in DCB by sonication for 1 h to obtain 1 mg mL^{-1} solutions. These solutions were used to study the interaction with TCNE.

Results and Discussion

We shall first discuss the results of ITC measurements on the interaction of graphenes with donor and acceptor molecules. Figure 1 shows typical data obtained with 1.0 mg mL^{-1} solutions of EG-A in toluene with TCNE and TTF. Raw ITC data for the blank titration of 10 mM TCNE and TTF against toluene are shown in Figure 1a and d. Figure 1b and e show the raw data for the titration of 10 mM TCNE and TTF solutions against 1.0 mg mL^{-1} EG-A solution. The ITC response in the TCNE and TTF titrations against EG-A is exothermic, as shown in Figure 1b and e. In order to eliminate dilution effects, heats from the blank titration data were subtracted from the molecule−graphene titration data. Figure 1c and f show the integrated heat changes (enthalpy changes in kcal mol^{-1}) after

TABLE 1: Energies of Interaction of Graphene and SWNTs with Electron Donor and Acceptor Molecules Obtained from ITC Measurements (in kcal mol^{-1})[a]

	EG-A[b]	HG[b]	SWNT[c]
TCNE	−5.88[d]	−4.2	−4.25
TCNQ	−0.24		−0.32
TNF	−0.12	−0.30	−0.06
DMPD	−0.40	−0.12	−7.4[e]
TTF	−0.07		−0.18

[a] The concentration of graphene and SWNTs was 1 mg mL^{-1} in all of the cases. [b] In toluene solvent. [c] In *o*-dichlorobenzene (DCB) solvent. [d] With DG-A, the value is −1.6. [e] This high value is due to interaction with the semiconducting SWNTs.

each injection of TCNE and TTF, respectively, after correcting for the heat of dilution. The exothermicity of the peaks reduces with progressive injection as the number of free sites for the binding of molecules available on the graphene decreases. The heat of reaction curve should ideally be sigmoidal in shape, but the limited solubility of graphene in toluene does not permit recording of the initial part of the sigmoidal curve. Absolute binding energies cannot therefore be obtained from the present data. The relative affinities of the different electron donor and acceptor molecules can, however, be estimated from the heat liberated in the initial injections, since all of the experiments were performed under similar conditions. The relative binding energies obtained from the initial points of the integrated heat plots in the case of EG-A and HG are listed in Table 1. The trend in the relative binding energies of electron acceptor molecules with EG-A obtained from ITC measurements is
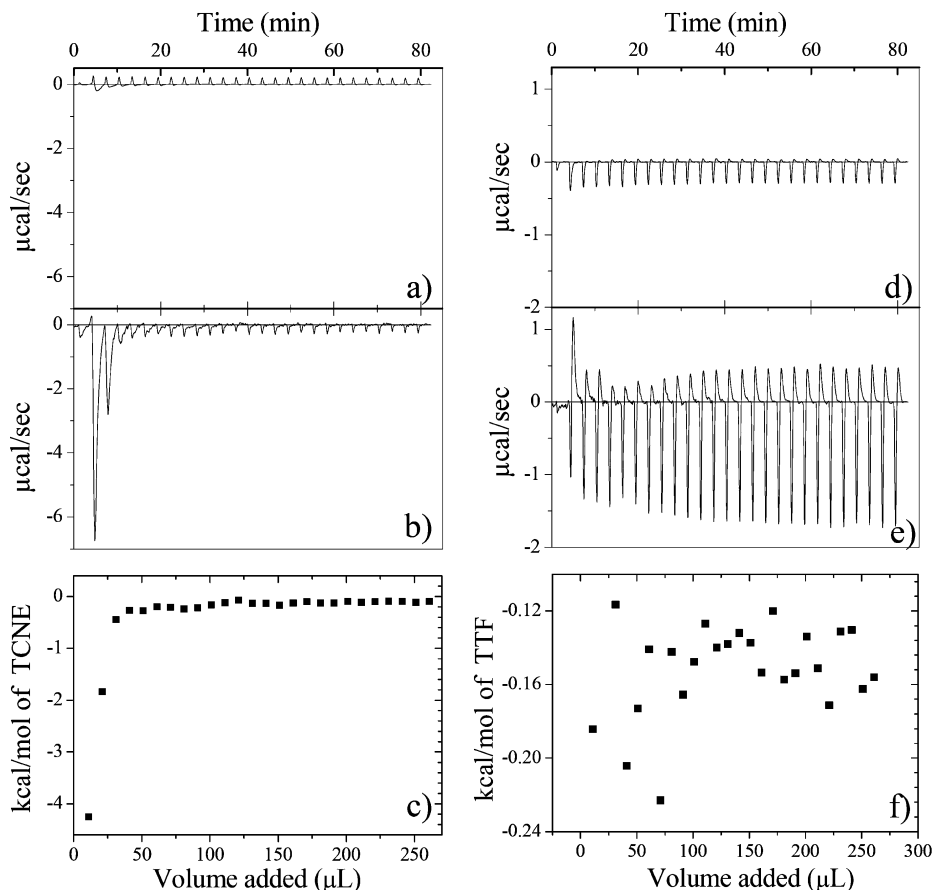
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Figure 2. ITC data recorded for the interaction of TCNE and TTF with SWNTs. ITC response for the blank titration with TCNE (a) and TTF (d). The raw ITC data for the titration of TCNE and TTF with 1.0 mg mL^{-1} of SWNT is shown in parts b and e. Parts c and f show the integrated heat of reaction at each injection for TCNE and TTF, respectively.

TCNE > TCNQ > TNF. Interaction energies of electron donor molecules with the graphene samples are considerably lower, the highest value being with *N,N*-dimethyl para-phenylenediamine (DMPD). The interaction energy of TTF is lower than that of DMPD. In the case of the interaction of TCNE with the different graphene samples, the highest ITC interaction energy is found to be with EG-A (−5.9 kcal mol^{-1}) and the lowest with DG-A (−1.6 kcal mol^{-1}). It is noteworthy that the surface area of EG is highest among the graphene samples.[17]

Interaction energies of graphene with different donor and acceptor molecules have been calculated by employing first-principles calculations using a linear combination of atomic orbital DFT methods implemented in the SIESTA package.[6] This study shows evidence for charge transfer between graphene and the donor and acceptor molecules. According to this study, the interaction energies of graphene with TCNE and TCNQ are greater than that with TTF. This is consistent with the results from our ITC studies. The calculations also show that a gap develops in the electronic structure of graphene on interaction with these molecules.

We have obtained ITC interaction energies of SWNTs with donor and acceptor molecules by a procedure similar to that with graphene by using *o*-dichlorobenzene (DCB) as the solvent. Typical data obtained for 1.0 mg mL^{-1} solutions of SWNTs in DCB interacting with TCNE and TTF are given in Figure 2, the raw data for the blank titration of 10 mM TCNE and TTF against DCB being shown in Figure 2a and d, respectively. Raw data for the titration of 10 mM TCNE and TTF solutions against the 1.0 mg mL^{-1} SWNT solution are given in Figure 2b and e. The ITC response in the titrations is exothermic, as revealed

by Figure 2b and e. The integrated heat changes after each injection of TCNE and TTF, respectively (after correcting for the heat of dilution), are shown in Figure 2c and f. Just as in the case of graphene, exothermicity of the peaks reduces with progressive injection. The energies of interaction calculated from the initial points of the integrated heat plots are listed in Table 1. It is interesting that, for electron acceptor molecules, the trend in the ITC interaction energies with SWNTs is the same as that with graphene (TCNE > TCNQ > TNF). Among the donor molecules, DMPD shows a higher interaction energy than TTF.

Since the data for SWNTs were obtained in DCB solvent, we wanted to compare the data of graphenes in the same solvent. The relative interaction energies of TCNE in DCB solvent are −1.4, −0.7, and −0.6 kcal mol^{-1} with EG-A, EG, and HG, respectively, giving the trend EG-A > EG > HG. This trend parallels that of the surface area. The interaction energy of SWNTs (−4.3 kcal mol^{-1}) with TCNE is generally larger than that for the graphene samples. First-principles calculations of Pati in this laboratory (personal communication) has shown the interaction energy of SWNTs with TCNQ to be greater than that with TTF. SWNTs exhibit a higher interaction energy than graphene.

Interaction energies of graphene as well as SWNTs with electron acceptor molecules increase progressively with the electron affinities of the acceptors, as can be seen in Figure 3a.[18] This result confirms that charge transfer between the acceptor molecules and graphene or SWNTs contributes significantly to the interaction energy. Indirect confirmation of this conclusion is also provided by the fact that the interaction energy varies systematically with the charge-transfer transition energy,
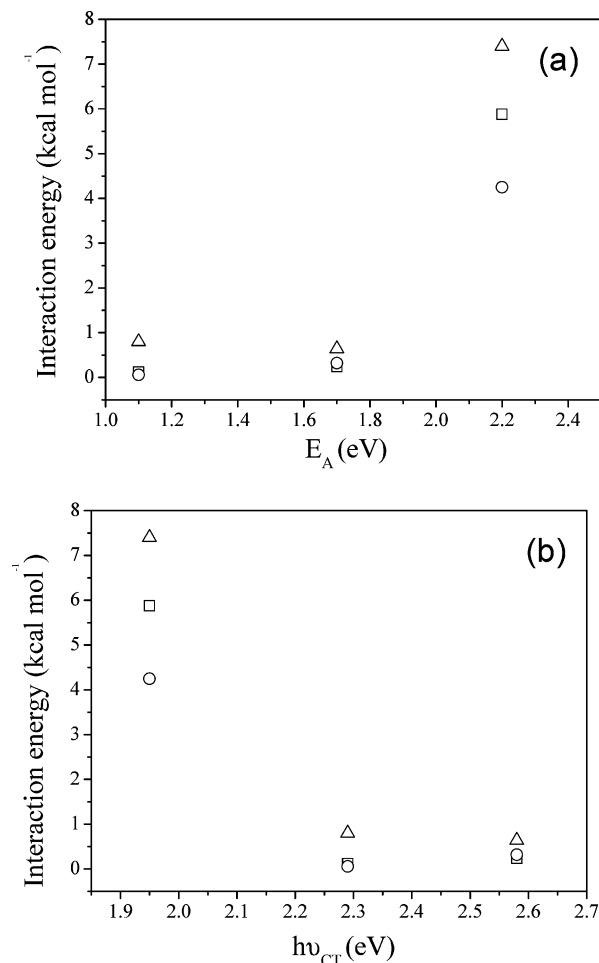
Figure 3. Variation of interaction energies of EG-A and SWNTs with electron acceptors (a) with the electron affinity of acceptors, E_A, and (b) with the charge-transfer transition energy, $h\nu_{CT}$, with anthracene (EG-A, squares; SWNTs, circles; metallic SWNTs, triangles).

TABLE 2: Energies of Interaction of SWNTs with Electron Donor and Acceptor Molecules Obtained from ITC Measurements (in kcal mol^{-1})^a

	SWNT^b	metallic SWNT
TCNE	−4.25	−7.4
TCNQ	−0.32	−0.64
TNF	−0.06	−0.80
TTF	−0.18	+0.07

^{a} The concentration of SWNTs was 1 mg mL^{-1} in DCB solvent in all of the cases. ^{b} Mixture containing 66% semiconducting and 33% metallic SWNTs.
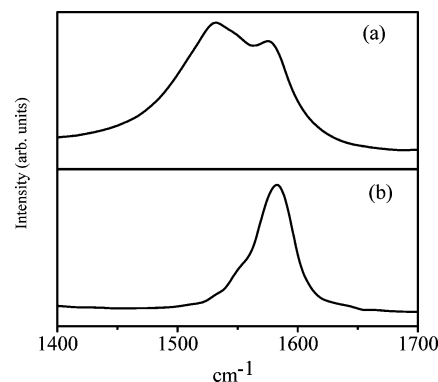

Figure 4. Raman G-band of (a) metallic SWNTs and (b) metallic SWNTs after interaction with TCNE (10 mM).

disappears completely and the band maximum shifts to 1582 cm^{-1}. This change in the Raman spectrum corresponds to the opening of a gap due to a change in the Fermi level of SWNTs, giving rise to an apparent metal-semiconductor transition. Electron-donating molecules have no effect on the Raman spectrum of metallic SWNTs. First-principles calculations also show that metallic (9,0) SWNTs develop a gap on interaction with TCNE. Electron-donating molecules, however, specifically interact with semiconducting nanotubes. Raman spectra show that semiconducting SWNTs exhibit an intense metallic feature in the 1540 cm^{-1} region on interaction with TTF.

Conclusions

In conclusion, ITC provides a satisfactory means to investigate the interaction of graphene as well as SWNTs with electron donor and acceptor molecules. Although ITC does not provide absolute interaction energies, it gives trends in interaction energy which are of value. Interaction energies of electron acceptor molecules (TCNE, TCNQ, and TNF) with graphene samples are higher than those of electron donor molecules (TTF and DMPD). Among the different graphene samples, the functionalized graphene EG-A shows the highest interaction energy. The studies carried out by us are on few-layer graphenes, but it would be somewhat difficult to investigate single-layer graphenes in this manner owing to its agglomeration in solid state. Interaction energies of SWNTs obtained from ITC are generally higher than those with graphene samples. Here again, TCNE gives the highest interaction energy. Metallic SWNTs interact reversibly with electron acceptor molecules, such as TCNE, the interaction energy being higher than with as-prepared SWNTs (containing a mixture of metallic and semiconducting species). On interaction of metallic SWNTs with TCNE, the metallic feature in the Raman G-band disappears, due to the opening of a gap through molecular charge transfer. It would be worthwhile to study the interaction of pure semiconducting SWNTs with donor and acceptor molecules by a combined use of ITC Raman spectroscopy.

$h\nu_{CT}$, of the acceptors with an aromatic such as anthracene,[19−21] as shown in Figure 3b.

SWNTs prepared by arc-discharge and other methods contain a mixture of metallic and semiconducting species,[9] the proportion of semiconducting nanotubes being around 66%. The interaction energies that we have given in Table 1 correspond to the mixture of metallic and semiconducting SWNTs. It would be more instructive if one were able to determine the interaction energy between the donor and acceptor molecules with pure metallic or semiconducting nanotubes. ITC measurements on the interaction of metallic SWNTs with donor and acceptor molecules reveal the interaction energy to be high in the case of TCNE (-7.4 kcal mol^{-1}), the energy varying in the order TCNE > TNF > TCNQ in the case of the acceptor molecules (Table 2). Interaction energies of acceptor molecules with metallic SWNTs are generally higher than those with the as-prepared SWNTs (containing the mixture of metallic and semiconducting species). The interaction energy of metallic nanotubes with a donor molecule such as TTF is negligible and could not be measured by ITC. This result shows that metallic nanotubes specifically interact with electron-withdrawing molecules. In order to understand the nature of this interaction, we examined the effect of acceptor and donor molecules on the Raman spectrum of metallic SWNTs. In Figure 4, we show the Raman G-band of metallic nanotubes before and after the interaction with TCNE (10 mM). On interaction with TCNE, the feature around 1540 cm^{-1} due to the metallic species[1,22]

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