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Synthesis of Nanocomposite Materials Using the Reprecipitation Method

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Abstract: Room temperature solution-based synthetic methods are an important option for the production of a wide range of nanomaterials. These methods often rely on self-assembly or self-organization of molecular precursors, with specific control of their nucleation and growth properties. We are developing strategies for the creation of multifunctional composite nanoparticles as well as models for predicting the bulk properties from the individual components and parameters of the processing conditions. One method of synthesis is a reprecipitation technique in which nanoparticle nucleation and growth is induced by the rapid injection of a molecular solution into a miscible non-solvent. Here we demonstrate that this method can be extended to multiple components, enabling the preparation of nanoparticles with multiple functionalities as well as materials with new properties arising from cooperative effects between the constituents. We synthesized nanocrystals of the charge transfer complex perylene:TCNQ (tetracyanoquinodimethane). Using the increase of the charge transfer band in the near infrared and dynamic light scattering data we try to develop a model for the formation and growth of these nanocrystals. By freeze drying the samples during growth and imaging with scanning electron microscope, we observe the morphologies of the crystals during their growth.

Keywords: Nanoparticles, charge-transfer, reprecipitation

1 Introduction

The study of nanomaterials has become commonplace in the research community. More than a decade after the initial buildup in nanoscience research [Drexler (1992)], and two thousand years since ancient Romans used gold nanoparticles to stain glass [Leonhardt (2007)], there is a wide range of synthetic methods for the creation of nanoparticles and nanofibers of various materials with controlled size and shape. Nanomaterials synthesis has progressed beyond the creation of

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single component, monofunctional substances. Complex multifunctional materials are being developed, for example, nanoparticle drugs that contain surface receptors for targeting and contrast agents for imaging [Torchilin (2006), Choi, Choi, Zhou and Kung (2003)]. Multiple component nanoparticles can also be important in enabling the combination of species that do not exist in isolated form, for example, the endohedral fullerene C_{80}:M_3N (M=transition metal); neither C_{80} nor the trimetallic nitrides are stable on their own [Stevenson, Rice, Glass, Marich, and Cromer (1999)].

An abundance of techniques exist for the synthesis of nanoparticles. These include vacuum techniques, precipitation, microemulsion, sol-gel, hydrothermal, templated, biomimetic, vacuum sputtering and consolidation methods [Cushing, Kolesnichenko, and Connor (2004), Puri (2004)]. In order to create specific particle architectures, molecular self-assembly and self-organization have been extensively looked at as a useful means of creating nanoparticles and other nanomaterials [Li, Schnablegger, and Mann (1999)] (by self-assembly we imply a designed molecular structure which gives interactions that cause a specific architecture to form). In these methods, a detailed understanding of interactions at the molecular level is needed in order to be able to predict the success of specific processing as well as tailor the properties of the resulting materials. These interactions can be in many forms: van der Waals, covalent, hydrogen bonds etc. To further complicate matters, the strength of these interactions can depend strongly on many variables such as concentration, temperature, pH, polarity, surface modification, solubility, etc.

One challenge is to develop general methods for making nanoparticles that enable a broad range of different types of multiple components to be combined in a predetermined way. In addition, there should be a straightforward way to scale the method up to production of industrial quantities. Along with this is the need for a better understanding of the relation between the molecular properties of the individual components, the specific synthesis and processing parameters and the final bulk material properties, so that materials can be engineered to yield desired functions.

We have been looking at the formation of nanoparticles using the solution-based reprecipitation method [Kasai, Nalwa, Oikawa, Okada, Matsuda, Minami, Kakuta, Ono, Mukoh, and Nakanishi (1992)], known alternately as solvent shifting [Texter (2001)], micronization [Horn and Rieger(2001)] or “drowning out” crystallization [Davey (1989)]. In this method, a solution of a particular molecular species (usually organic and nonpolar) is prepared and then rapidly mixed with a miscible non-solvent such as water. The solubility of the solute decreases rapidly, usually inhomogeneously and over various time scales. The molecules aggregate and form nanoparticles. For example, by adding an acetone solution of the chemicals naphthalene or Magnesium phthalocyanine to water, we can induce the formation of nanoparticles with crystalline order (nanocrystals), which can be stabilized against further growth by the addition of surfactants [Van Keuren, Georgieva, and Adrian (2001)]. Despite the lack of precise control over the molecular self-organization, the nanoparticles usually have a narrow size distribution.

Often the solution is in a water miscible solvent such as acetone or ethanol, which is rapidly injected into water, but other variations have also been used, such as "inverse" reprecipitation of water soluble molecules by injection into more nonpolar solvents. The reprecipitation method has been used in various forms to produce optical materials [Yokoh and Ogata (1992)], polymers [Watanabe, Yamada, and Ogata (1995)], organic nanocrystals [Baba, Kasai, Okada, Oikawa, and Nakanishi (2003)], and provitamins [High and Day (1952)]. The last of these is important because it demonstrates the scalability of the method to industrial levels; BASF produces large quantities of beta carotene nanoparticles and related materials per year for use as vitamin additives.

This method works well for single component nanoparticles. Creating nanoparticles containing multiple components using this method is not as simple, although the many potential applications for multifunctional nanoparticles make this a promising area of research [Katz and Willner (2004)]. In order to get the various components to assemble into single nucleation sites, the solubilities of the components in both solvents as well as their interactions with each other need to be understood. Some work has been done in creating specific composite nanoparticles with this method. Pu et al. demonstrated coprecipitation of microparticles of the cancer drug 5-Fluorouracil with poly(L-actide) using supercritical CO_2 [Pu, Kang, Chen, Liao, and Yin (2007)]. Other groups have developed electrochemical coprecipitation methods for synthesizing biomolecular nanocomposites [Zhang, Xi, and Chen (2008)].

At a basic level, many of the same issues are faced by crystal growers attempting to co-crystallize materials. While inducing a phase transformation requires only a reduction in the free energy of one phase with respect to the other, co-crystallization of two or more components involves the interactions between the two components as well as each with the solvent.

Here we demonstrate the ability to co-crystallize nanoparticles of the charge transfer molecular crystal perylene:TCNQ using reprecipitation.

2 Background and Theory

A comprehensive understanding of the nucleation and growth of nanoparticles in the reprecipitation method requires a consideration of both kinetics and thermodynamics. The fact that the formation occurs in an inhomogeneous and rapidly varying environment complicates the analysis. However, continued interest in this method in academia and industry has resulted in progress in the developments of models for the particle formation.

2.1 Classical nucleation theory

The nucleation and growth of a solid phase from a solution can be approached from a number of perspectives. At a macroscopic level, a thermodynamic picture can be considered in which the nucleation is simply a first order phase transition [Kashchiev (2000)]. When a solution is slowly brought to supersaturation, it enters a metastable region in which separation into two phases is energetically favorable, but where an energy barrier prevents immediate nucleation of particles. This barrier is due to a positive free energy contribution for molecules at the particle's surface, and results in a critical radius, below which clusters of molecules may form, but they will not be large enough to be kinetically stable. As the concentration is further increased, this energy barrier will be overcome by the higher solute concentration and at some point, the system undergoes a first order phase transition and stable particles will form [Oxtoby (1998)]. This description is a basic starting point for the development of the thermodynamics of crystallization [Mullin (2001)].

On a molecular level, as the two solvents are mixed during the reprecipitation, the solute sees fewer and fewer "favorable" solvent molecules in its vicinity with which it can associate, and eventually begins to self organize with similar species. For a slow increase in the supersaturation, this should happen according to the standard models of phase transitions. However, in reprecipitation the system is far from equilibrium. Despite this, it been shown by Mori et al. [Mori, Miyashita, Oliveira, Oikawa, and Nakanishi (2009)] that the nucleation and growth can be accurately described using classical nucleation theory, which gives the rate of nanoparticle formation as a function of the degree of supersaturation. It is likely that while the initial nucleation is heterogeneous, the later stages of growth of the nanoparticles occur under quasi-equilibrium conditions, since the nucleation and growth of particles reduces the concentration of solute. In these later stages, the solution approaches a homogeneous system nearly in equilibrium with the solid nanoparticle phase, with growth by molecular diffusion to the particle surface.

This model of a rapid nucleation "burst" followed by slower diffusion-limited growth was originally proposed by LaMer and Dinegar as a way to understand the very narrow size distributions that result from these types of synthetic methods [LaMer and Dinegar (1950)]. Reiss later showed that diffusional growth itself resulted in a further narrowing of size distributions [Reiss (1951)]. While later work has shown that the situation is often more complex [Matijevic (1994)], the basic ideas can still be applied for a general understanding of nucleation and growth of nanocrystals in this method. However, for the co-crystallization of multiple components the additional complexity introduced by the interactions between the different species must be taken into account.

2.2 Co-crystallization and solubility

A starting point for considering whether two components co-crystallize is the use of solubility parameters. The Hildebrand solubility parameter is a value that is related to the free energy required to remove a single molecule of a material from a crystal to an isolated state [Hansen (2000)]

$$\delta = \sqrt{\frac{\Delta H - RT}{V_m}} \tag{1}$$

where ΔH is the heat of vaporization, R is the gas constant, T is the temperature and V_m is the molar volume. It has been shown that the miscibility of two materials is often related to how close their solubility parameters are to each other. Work by Nakanishis's group on composite nanoparticles (polymers containing porogens) corroborates this for the case of co-aggregation of polymer precursors and porogens [Zhao, Ishizaka, Okada, and Nakanishi (1998)]. The temperature dependence can be used to adjust the values of the two parameters in order to increase the likelihood of co-crystallization. More complex analysis of solubility leads to multivalued solubility parameters such as Hansen's parameters [Hansen (2000)], which consider separate contributions from hydrogen bonding, dispersion and polar effects.

The initial formation of a particle will depend critically on the relative interactions between the two or more solutes, the solvent(s) and solute and the solvent molecules with each other. On the microscopic scale, the solubility of a particular chemical species can be considered in terms of the interaction strength with the solvent and with other solute molecules, both relative to the thermal energy kT. If this energy is larger than both, the solute should be soluble - the thermal activation will prevent long term association of molecules. If kT is smaller, and if the interaction between solute and solvent is stronger than between solute molecules, the solubility will also be large, since the solute molecules will preferentially associate with the solvent rather than each other. If the opposite is true, the solute molecules will self associate and lead to phase separation. This is all for the case of very dilute samples. As the concentration increases, the average strengths of the solute-solute and solute-solvent interactions will be altered. At the point where these changes affect the relative interactions, the saturation point will be reached.

The formation of single component nanoparticles in these terms is straightforward. After mixing, the solubility of the solute in the new solvent is greatly reduced, causing the molecules to associate into particles. For more than two components (two solutes and solvent) the situation is more complicated. There are multiple interaction strengths to consider. As was the case for the single solute, if kT is larger than all interactions, then there should be mutual solubility (single phase).

These are all considerations in the thermodynamic limit. The heterogeneous particle formation during mixing may affect the actual types of particles that form. There is also the assumption that the remaining amount of good solvent can be ignored, but this may not be valid. We need to consider, for example, whether the good solvent can form a solvent cage around one or both species and what the affect would be. The development of these models will be aided by the statistical design of experiment methods described above in order to determine critical parameters that influence nanoparticle formation.

Temperature and initial concentration are two obvious factors that will dictate the particle formation. Temperature enters the co-solubility directly in affecting the value of the solubility parameter as in Eq. 1, but also indirectly in influencing the solubility of the individual components in the solvent. It has been shown that temperature plays a significant role in the growth of nanoparticles of perylene prepared using the reprecipitation method [Kasai, Oikawa, Okada, Nakanishi (1998)].

Concentration has also been shown to play a large role in the size of single component nanoparticles prepared with reprecipitation [Horn and Rieger (2001)]. We have shown a strong nonlinear dependence of particle size on concentration of Magnesium phthalocyanine nanoparticles prepared with reprecipitation [Van Keuren, Bone, and Ma (2008)]. In the case that nanocrystals can be formed from multiple components, there will be the additional matter of obtaining the correct stoichiometry of the crystal - depending on the interactions, this may not result from a strict molar ratio in the initial solutions.

Other conditions will also likely play a role in the reprecipitation of composite nanoparticles as they do for single component ones. Besides the van der Waals forces, which are the primary interactions at long range, hydrogen bonding and electrostatic (charge and dipole) interactions will influence the formation and stability of the particles.

2.3 Charge transfer crystals

Charge transfer complexes are formed by donor-acceptor interactions and can consist of either two organic molecules or an organic molecule with an inorganic molecule. The transfer creates unique optical and electronic states that do not exist in the individual components. The ability to monitor the formation of charge transfer compounds using their optical spectra makes them useful for demonstrating the possibilities of co-crystallization of composite nanoparticles. Single component nanoparticles of charge transfer compounds have been prepared, for example, the material CuTCNQ [Hiraishi, Masuhara, Yokoyama, Kasai, and Nakanishi (2008)].

The electron acceptor tetracyanoquinodimethane (TCNQ) forms charge transfer molecular crystals with a number of aromatic, electron donating molecules such as perylene [Shokaryev, Buurma, Jurchescu, Uijttewaal, De Wijs, Palstra, and Groot (2008)], tetrathiafulvalene (TTF) [Tokiewicz, Engler, and Schultz (1975)] or tetracene [Shokaryev, Buurma, Jurchescu, Uijttewaal, De Wijs, Palstra, and Groot (2008)]. In addition to their use as model system, charge transfer nanocrystals may be suited to various practical applications. When the electron donating molecule perylene is crystallized together with the electron acceptor TCNQ (tetracyanoquinodimethane), the resulting charge transfer crystal is reported to have high mobilities for both holes and electrons, which could make it a useful electronic material [Shokaryev, Buurma, Jurchescu, Uijttewaal, De Wijs, Palstra, and Groot (2008)]. This suggests that the electronic properties of the nanocrystals could also be useful, for example, in devices such as organic solar cells, where charge transport can be as important as energy conversion in obtaining high efficiency devices [Ross, Cardona, Guldi, Sankaranarayanan, Reese, Kopidakis, Peet, Walker, Bazan, Van Keuren, Holloway, and Drees (2009)]. In addition, the co-crystal is reported to have very low band gaps as well as absorption peaks in the infrared which do not exist in perylene and TCNQ individually [Troung and Bandrauk (1976), Michaud, Hota, and Zauhar (1976)].

2.4 Optical characterization of nanocrystals

The onset of this self-organization can be monitored in a number of ways, such as in the optical and electronic characteristics. In particular, changes in the optical absorption spectra, especially the appearance of new absorption bands, can be related to the growth of organized structures. Much of the early work on nanoparticle synthesis by reprecipitation used optical spectra as indicators of nanocrystal formation, for example, Kasai et al. used optical absorbance spectra of water dispersion of perylene crystals prepared by the method to show its size dependence and compared them to that of acetone solutions of perylene to show the shift in the excitonic absorption peak of crystals [Kasai, Kamatani, Okada, Oikawa, Matsuda, and Nakanishi (1996)]. In addition, fluorescence quenching has long been used as a measure of the association of two or more emitting species. For molecules that normally lose excited state energy by fluorescence emission, the association with one or more other molecules provides other pathways for de-excitation, such as intermolecular vibrational states and resonant energy transfer. This results in strong quenching of fluorescence when molecules form dimers or larger assemblies.

Optical spectroscopy can also be a valuable tool for investigating cluster formation.

The key point for inferring cluster formation in both of these materials is the significant spectral change between molecular and crystalline forms. For example, new bands appear in the low temperature absorption and fluorescence spectrum of perylene as it dimerizes [Weiss, Kietzmann, Mahrt, Tufts, Storck, and Willig (1992)].

In addition to the use of spectra as indicators of crystal formation, much of the work in developing these types of materials stems from the desire to achieve enhanced linear or nonlinear optical properties due to the nanoscale size effects. Nanoparticles have been investigated as nonlinear optical materials, both for the enhancement due to the quantum mechanical effect of the confinement of the electrons in the particles as well as the ability to fabricate good optical quality materials by doping glass or homogeneous polymers with optically active nanoparticles. We have seen enhancement in the nonlinear optical properties of a number of types of nanoparticles such as gold [Schrof, Rozouvan, Van Keuren, Horn, and Schmitt (1998)], polydiacetylene [Matsuda, Yamada, Van Keuren, Katagi, Kasai, Okada, Oikawa, Nakanishi, Smith, Kar, and Wherret (1997)] and merocyanine dye J-aggregates [Matsuda, Van Keuren, Masaki, Yase, Mito, Takahashi, Kasai, Kamatani, Okada, and Nakanishi (1995)].

3 Experimental Methods

Samples are prepared using the reprecipitation method [Kasai, Oikawa, Okada, and Nakanishi (1998)]. Perylene was purchased from Sigma-Aldrich and 7,7,8,8-Tetracyanoquinodimethane (TCNQ) was purchased from Acros Organics. Both are used without further purification and individually dissolved in acetone at a concentration of 2.5 mM. For the co-crystallization of nanoparticles, a 1:1 molar ratio of perylene and TCNQ are mixed together, and the acetone solution of perylene:TCNQ is rapidly injected into distilled water using a microsyringe and vigorously stirred usually at room temperature. To compare the multicomponent nanoparticles with those made from the individual components, nanoparticles of perylene and TCNQ were prepared using the same method. All of the acetone solutions are mixed with water at 1:9 (acetone:water) ratio where 200 μm of acetone solution is injected in to 1.8 ml of distilled water.

To characterize the co-crystallized nanoparticles, we employed several different methods. In order to examine the particle growth, dynamic light scattering (DLS) was used. By observing temporal fluctuations in elastically scattered light intensity due to Brownian motion of particles, this method determines diffusion coefficients of nanoparticles and from those, an effective particle size (diameter) d is calculated using the Stokes-Einstein relation:

$$D = \frac{k_B T}{3\pi\eta d} \tag{2}$$

where D is the diffusion coefficient, k_B is the Boltzmann constant, T the absolute temperature, and η the viscosity of the sample solution.

With excitation from a 10 mW HeNe laser (JDS Uniphase 1202-1), the intensity fluctuation signals of scattered light from a sample are collected by a single mode optical fiber, which is coupled to an avalanche photodiode detector (Perkin Elmer SPCM CD2882), which is oriented to collect scattered light at 90° with respect to the incident laser. The collected signals are input to an ALV-5000 Multiple Tau Digital Correlator and the photon count autocorrelation functions analyzed using a nonlinear fitting routine programmed in Matlab. The exact expression for the autocorrelation function given by Frisken [Frisken (2001)] was used to model the data. For each run, the sampling time was set to 30 seconds, and the DLS measurements were taken continuously for several hours starting right after mixing.

We also used absorption spectroscopy as a major tool in identifying the presence of the charger transfer compound in the co-crystallized nanoparticles. Absorption spectra of a sample were acquired by a spectrophotometer (Ocean Optics CHEM2000-UV-VIS) in the wavelength range 350 to 1000 nm. A solution of acetone and water with the same ratio as the solvent for the nanoparticle samples (1:9 ratio) is used as a reference.

To investigate the change in the charge transfer compounds, Raman spectroscopy is employed as well. Raman Spectra of a sample were obtained by a Raman spectrometer (Renishaw RM 1000) equipped with a CCD detection with a 514.5 nm Ar laser or a 785 nm diode laser excitation.

Finally, scanning electron microscopy (SEM) was employed to image the co-crystallized nanoparticles. The dispersions of co-crystallized nanoparticles were rapidly frozen with liquid nitrogen and then freeze dried 40 minutes after reprecipitation for SEM. For SEM imaging, a Zeiss Supra 55VP was used with an in-lens detector at the working distance of 4 mm and with an aperture of 30 μm and 4 to 10 kV acceleration voltage.

4 Results and Discussion

Dynamic light scattering (DLS) measurements of the particle size showed rapid formation of particles of perylene:TCNQ, which increased in size (diameter) from roughly 200 nm to 450 nm, a size at which they remained stable for several hours. Figure 1 shows that particles of perylene:TCNQ are larger than that of perylene, which reached sizes on the order of 200 nm fifteen minutes after reprecipitation. This indicates the likelihood that the particles formed were of the mixed material, since particles with only perylene formed smaller particle sizes than the size of perylene:TCNQ. We also attempted to observe particle growth vs. time of TCNQ using DLS. However, because TCNQ can rapidly form large microcrystalline structures which can intermittently enter the sampling volume and scatter strongly, consistent autocorrelation functions could not be obtained and hence are not included in the figure.

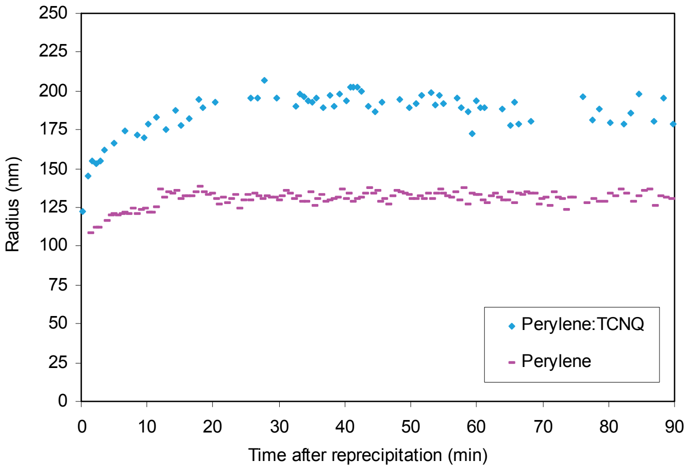

Figure 1: Particle growth of perylene:TCNQ and perylene measured by DLS

Figure 2 shows the absorption spectra of nanoparticles of perylene, TCNQ and a 1:1 molar ratio of perylene and TCNQ. The most noticeable feature appearing in the mixed component sample is the broad infrared peak centered around 920 nm. Such an absorption peak is observed in crystals of perylene and TCNQ and is attributed to the charge transfer state [Troung and Bandrauk (1976), Michaud, Hota, and Zauhar (1976)]. Its appearance in the nanoparticles suggests the formation of the composite nanocrystals, rather than nanoparticles of the individual components or an amorphous composite nanoparticle.

The charge transfer absorption arises from the dimer of perylene:TCNQ, which is likely to be the initial structure formed. This change in the spectrum occurred rapidly (<1 second) after mixing, suggesting that dimerization occurs quickly. Stop-flow experiments on perylene nanocrystals by Mori et al. indicated that spectral changes due to molecular assembly to form crystals occurs within milliseconds after mixing.

Figure 3 shows Raman spectra of powder samples of perylene, TCNQ and the mixed nanocrystals. The sensitivity of many vibrations to the local environment causes shifts in IR and Raman lines between the pure compounds and the corre-

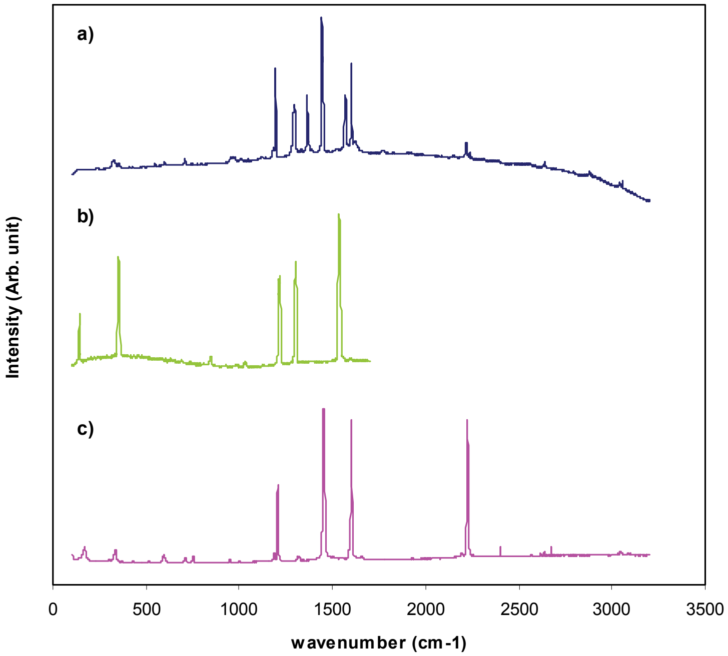

Figure 2: Absorption spectra of nanoparticles of (a) perylene, (b) TCNQ and (c) a 1:1 molar mixture of perylene:TCNQ prepared with the reprecipitation method.

sponding lines in the charge transfer crystal. These can be observed in the spectra. While some lines are unaffected, for example the 1602 cm^{-1} line in TCNQ, corresponding to the C=C ring stretching and CH bending [Paqlukojc, Natkaniec, Bator, Sobczyk, and Grech (2003)], does not shift in the nano-co-crystal. However, other lines such as the 1216 cm^{-1} line in perylene, attributed to in-plane CCH bending [Ong, Jensen, and Hameka (1999)], and the 1208 cm^{-1} line in TCNQ, due to CH bending [Paqlukojc, Natkaniec, Bator, Sobczyk, and Grech (2003)], show significant spectral shifts in the perylene:TCNQ co-crystal due to interactions with their environment.

Scanning electron microscope images corroborate the DLS, absorption and Raman data and show crystal habits in the co-crystal (Figure 4) that are not observed in similar images of perylene (Figure 5) or TCNQ (Figure 6-7) nanocrystals only. Polyhedral structures of perylene:TCNQ nanocrystals have morphologies somewhat similar to perylene nanocrystals but that are in general slightly larger. TCNQ structures appeared in a wide variety of other forms with a wide variety of size scales, such as rhombic plates and dendritic structures [Melinger, Laman, Harsha,

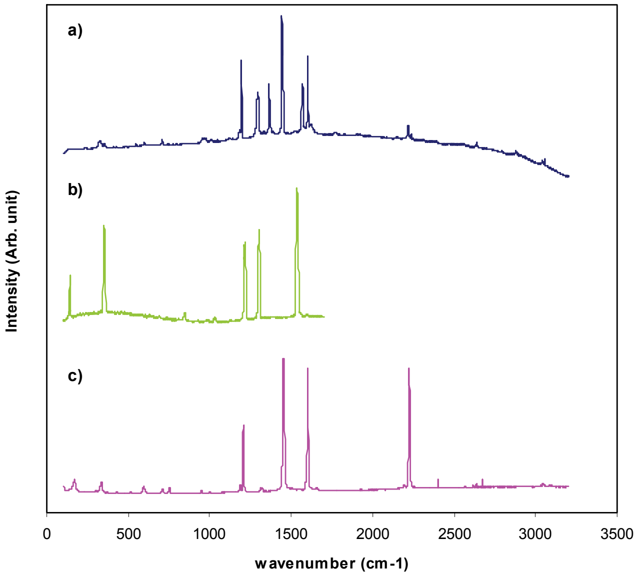

Figure 3: Raman spectra of (a) a 1:1 molar mixture of perylene:TCNQ prepared with the reprecipitation method at the 514 nm excitation, (b) perylene powder (no reprecipitation) at 785 nm excitation, and (c) TCNQ powder (no reprecipitation) at 514 nm excitation. The longer wavenumber data in perylene was removed during background subtraction – no spectral features were observed above 1700 cm^{-1}.

Cheng, and Grischkowsky (2007)], none of which have any resemblance to the perylene:TCNQ structures. Perylene:TCNQ resembles perylene in shape; however, while perylene generally appears to be cuboid shape, perylene:TCNQ are rhombohedron and some have more faces.

5 Conclusion

We have demonstrated the successful preparation of mixed charge transfer nanocrystals of perylene:TCNQ using the reprecipitation method. The onset of this self-organization can be monitored by a number of characterization methods. These nanocrystals form and stabilize quickly, within approximately 30 minutes. Nanocrystal sizes in the range of several hundred nanometers were found by dynamic light scattering and cryo-scanning electron microscopy. The presence of the charge transfer crystal is inferred from the absorption and Raman spectra.

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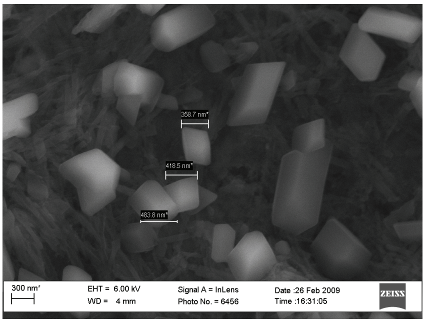

Figure 4: SEM images of perylene:TCNQ nanocrystals

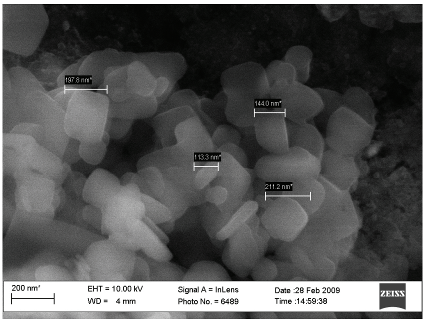

Figure 5: Typical perylene nanocrystals formed by the reprecipitation method.

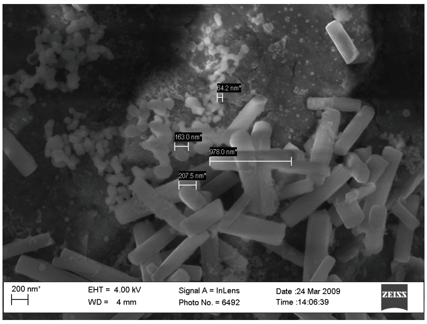

Figure 6: One type of the structures observed in a freeze-dried sample of TCNQ nanocrystals.

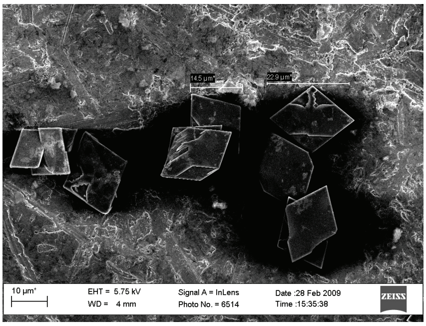

Figure 7: Rhombic plates of TCNQ

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