ON THE CARRIER OF THE EXTENDED RED EMISSION AND BLUE LUMINESCENCE

S. WADA, Y. MIZUTANI, T. NARISAWA, AND A. T. TOKUNAGA

1 Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofugaoka, Chofu, Tokyo 182-8585, Japan; wada@pio.jp
2 Center for Instrumental Analysis, Chofugaoka, Chofu, Tokyo 182-8585, Japan
3 Institute for Astronomy, University of Hawaii, 2680 Woodlawn Dr., Honolulu, HI 96822, USA

ABSTRACT

Filmy-QCC, an organic material synthesized in the laboratory, exhibits red photoluminescence (PL). The peak wavelength of the PL ranges from 650 to 690 nm, depending on the mass distribution of polycyclic aromatic hydrocarbon (PAH) molecules, and the emission profile is a good match for that of the extended red emission (ERE) in the Red Rectangle (RR) nebula. The quantum yield of the PL ranges from 0.009 to 0.04. When filmy-QCC is dissolved in cyclohexane, it exhibits blue PL in the wavelength range of 400–500 nm with a quantum yield of 0.12–0.16. The large width of the red PL and the large wavelength difference between the PL of the filmy-QCC as a solid film and in a solution indicate that there is a strong interaction between the components of filmy-QCC. The major components of filmy-QCC are PAHs up to 500 amu. Our laboratory data suggest that the blue luminescence observed in the RR nebula is probably caused by small PAHs in a gaseous state, and the ERE is caused by larger PAHs in dust grains.

Key words: astrochemistry – dust, extinction – methods: laboratory – stars: individual (Red Rectangle, HD 44179) – techniques: spectroscopic

1. INTRODUCTION

Extended red emission (ERE), a broad red emission band at 540–950 nm, was first observed in the Red Rectangle (RR) nebula by Cohen et al. (1975). ERE of different widths and central wavelengths was found in reflection nebula (Witt & Boroson 1990), planetary nebula (Furton & Witt 1992), compact H II regions (Darbon et al. 2000), and the interstellar medium (Gordon et al. 1998). Darbon et al. (1999) showed that the peak wavelength of the ERE varies from 650 to 780 nm in these objects. They also showed a correlation between the width and the peak wavelength of the ERE band in the sense that the width of the ERE increases from 60 to 120 nm as the ERE peak shifts from 650 to 780 nm. Smith & Witt (2002) showed that the ERE peak wavelength is shifted toward longer wavelengths with increasing far-UV radiation density, consistent with the results of Darbon et al. (1999). Witt & Vijh (2004) summarized the observations and proposed constraints for ERE carriers from observations, and Witt et al. (2006) added further observational constraints.

The ERE arises from photoluminescence (PL). Experiments have shown that various materials emit red luminescence. However, it is thought that a specific class of material gives rise to the ERE. Many candidates for the carrier have been proposed, for example, polycyclic aromatic hydrocarbons (d’Hendecourt et al. 1986, PAHs), quenched carbonaceous composite (Sakata et al. 1992, QCC), hydrogenated amorphous carbon (Furton & Witt 1992, HAC), carbon clusters (Seahra & Duley 1999), crystalline silicon nanoparticles (Ledoux et al. 2001), nanodiamonds (Chang et al. 2006), and doubly ionized PAH ions (divalent cations) (Witt et al. 2006). Koike et al. (2002) have also suggested that the ERE is caused by thermoluminescence of silicates. Ledoux et al. (1998, 2001) showed that crystalline silicon nanoparticles have a high-PL quantum yield compared with other candidate materials and that the PL quantum yield is a very significant physical constraint for candidate materials.

Recently, blue luminescence (BL) was detected in the RR (Vijh et al. 2004) and other reflection nebulae (Vijh et al. 2005b). In contrast to the ERE, Vijh et al. (2005b) show that the BL has about three components and they suggested small neutral PAHs in the gas phase (three- and four-ring PAHs) could explain the BL. In addition, Vijh et al. (2006) suggest that the BL and the ERE arise from the same family of carriers in different ionization states.

The RR nebula is illuminated by HD 44179, which is a binary star. The RR nebula shows many dust features from the ultraviolet to the infrared spectral region, namely the intense BL and ERE as well as the infrared emission bands of carbonaceous materials referred to as the PAH bands, unidentified infrared (UIR) bands, aromatic emission features (AEF), or infrared emission features (IEF) (Sellgren 2001). There are also sharp emission spikes overlaid on the ERE, some of which are close in wavelength to the diffuse interstellar absorption bands (Scarrott et al. 1992; Duley 1998).

One hypothesis that we explore here is that the BL, ERE, and IEF arise from related materials. Sakata et al. (1992) synthesized a candidate material, filmy-QCC, from a methane plasma to explain the ERE. The PL from the filmy-QCC shows a single broad feature with a peak wavelength and width similar to that of the ERE. Filmy-QCC also has infrared absorption bands that are similar in wavelength to the observed IEF. The filmy-QCC is thought to be a mixture of various organic molecules, but Sakata et al. (1992) did not carry out a precise analysis of the chemical composition. They also showed that filmy-QCC dissolved in a solution of Freon emits luminescence with a blue–green color with a yellow tint.

In this paper, we present additional experiments on filmy-QCC and show (1) new data on the chemical composition of the filmy-QCC and (2) absorption spectra, PL spectra, and PL quantum yield measurements of filmy-QCC as a solid and dissolved in cyclohexane. We discuss the evidence that filmy-QCC is a possible laboratory analog for the ERE carrier and that small PAH components are the BL carrier in the RR.
2. EXPERIMENTS AND RESULTS

2.1. Preparation of Filmy-QCC

The preparation method of the filmy-QCC was the same as described in previous papers (Sakata et al. 1992, 1994). Methane was used as a source gas, and when it was irradiated by microwaves in a quartz chamber, a plasma was formed. Emission lines of atomic H, CH, C₂, and C₃ were detected in the emission from the plasma. The plasma was ejected through a nozzle into a vacuum chamber. The nozzle had a diameter of 1 mm and a length of 7 mm. Mass peaks of CH₄, C₂H₂, C₂H₄, C₃H₂, C₆H₆, and C₆H₆ were detected in the ejected gas by monitoring with a quadrupole mass spectrometer. A filmy deposit, named filmy-QCC, condensed on a substrate of synthetic quartz glass set on the wall of the vacuum chamber. The formation of filmy-QCC involves the quenching of hot gases consisting of hydrocarbon radicals. As a result, when first formed under vacuum, filmy-QCC is highly reactive with oxygen under UV radiation, and special care in handling is required. The filmy-QCC sample deposited near the nozzle was brown in color, and the samples collected far from the nozzle were yellow. Thus the composition of the filmy-QCCs changed depending on sampling location. Another type of deposit, named dark-QCC, formed on the substrate directly in the gas beam from the nozzle. The color of the dark-QCC was black. The material is a carbonaceous material with an onion-like structure. A detailed description of the nature of QCC materials is given by Wada & Tokunaga (2006).

Emission from CH, C₂, and C₃ were present, and we also detected mass peaks of CH₄, C₂H₂, and C₆H₆ in the gas ejected from the plasma. Recently, Roesler et al. (2003) reported that the addition of ethane to source gases increases PAH production in a combustion flame. They suggested that the increase of methyl radical formation (one carbon atom species) helps to produce PAHs. Siegman & Sattler (2000) also show that acetylene (a two-carbon atom species) is an important species for the growth reaction of PAHs. Based on this, we think that both C₁ species (such as C, CH, CH₂, CH₃, CH₄, and their ions) and C₂ species (such as C₂, C₂H, C₂H₂, C₂H₃, C₂H₄, and their ions) are necessary for PAH formation.

The filmy-QCC was deposited on the substrate from the gases ejected through the nozzle of the plasma chamber. The substrates were set at 5, 15, 25, and 35 mm from the nozzle of the plasma chamber. The temperature of the substrates was elevated during the collection of the QCC material and was measured to be about 170, 110–130, 90, and 65 °C, respectively. Two kinds of growth reactions are possible. One is the addition reactions of PAHs to each other, and the other is addition reactions of small radicals to PAH molecules. The presence of two mass groups in the gas evaporated from the dark-QCC. These two envelopes are possibly formed by dimerization.

3. The central mass of the envelope decreases as the distance of the sampling location from the nozzle increases. The central mass is at 398 amu at 5 mm and 252 amu at 70 mm. Larger molecules are therefore formed in the deposit closer to the nozzle.

4. Although we propose candidate molecules from the mass spectra, we cannot determine the precise molecular composition of the filmy-QCC by only mass analysis. For example, molecules that could match the 252 amu peak (C₃₀H₁₂) include benzo(a)fluoranthene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(e)pyrene, perylene, etc. (see, for example, Allamandola et al. 1999, Figure 1). Therefore, we cannot determine the chemical composition by mass spectra alone.

5. The major mass peaks of the filmy-QCCs are comparable in amu to compact PAHs (pericondensed PAHs) such as coronene (C₂₄H₁₂, 300 amu), ovalene (C₃₂H₁₄, 398 amu), circumplatinene (C₃₈H₁₆, 472 amu), circumanthracene (C₄₀H₁₆, 496 amu), and cumiperylene (C₄₂H₁₆, 520 amu). Long PAHs (catacondensed PAHs) contain more hydrogen atoms than the pericondensed PAHs. However, the long PAHs are not a major component of the filmy-QCC.
are not planar. Curved and parallel structures are often observed in the TEM images of the filmy-QCC (Wada et al. 1999; Goto et al. 2000). Therefore, we included five-membered carbon rings together with flat PAHs, dihydro-PAHs, and substituted PAHs.

The PAH molecules in the filmy-QCC are probably stacked parallel to each other and displaced laterally. Aliphatic side groups of PAHs and hydrogenated PAHs will disturb the arrangement of the molecules. Therefore, the distance between the planes of the stacked PAHs will be wider than the interlayer distance of graphite.

A. Sakata (1992, private communication) measured the mass spectra of gases evaporated from the filmy-QCC during heating. The major mass peaks Sakata observed can also be explained by various types of PAHs. But his mass spectra contained more dihydro-PAHs and substituted PAHs than the mass spectra shown in Figure 1. One reason is the different ionization method for the mass analysis (electron impact in Sakata’s analysis and photoionization in this paper). A second reason is that chemical reactions in the film can occur during gradual heating in Sakata’s experiment.

2.3. Absorption Spectroscopy

The filmy-QCC was collected on a quartz glass set at different distances from the nozzle of the plasma chamber. Absorption spectra of the filmy-QCCs and their solution were measured by a U-3300 UV-VIS spectrophotometer (Hitachi Co.). As shown in Figure 3(a), the absorbance peak of the filmy-QCC as a solid condensed at 20 and 27 nm from the nozzle has two strong peaks located around 210–230 and 310–320 nm. However, the absorbance of the samples collected at 5 and 13 mm are composed of two peaks at 220–230 and 370–380 nm. Other small absorbance peaks are found in the 400–500 nm region.

We also measured the absorbance spectra filmy-QCC dissolved in cyclohexane, and these are shown in Figure 3(b). The peaks in the shortest-wavelength region are located at about 200 nm. They are shifted to shorter-wavelength region than those in the filmy-QCC spectra shown in Figure 3(a). Peaks observed at 310–320 and 370–380 nm in the film spectra are observed at 300 and 350 nm in the solution spectra. The shift of the bands between the film spectra and solution spectra demonstrates the presence of molecular interactions in the solid filmy-QCC components.

The absorbance peak caused by the S0 to S1 transition (S1 ← S0) is located at longer wavelengths in PAHs. It is located at 369 nm in the spectrum of fluoranthene (C16H10) and at 372 nm in pyrene (C16H10). In the spectrum of circumanthracene (C40H16), an absorbance peak is observed at 612 nm (Clar 1964). Larger PAHs usually show an absorbance peak at a longer wavelength. Ovalene (C32H14) in an isolated state shows absorbance peaks of S1 ← S0 in the range of 466–430 nm and peaks of S2 ← S0 at 430–425 nm (Amirav et al. 1981).

In general, this trend of larger PAHs (higher mass peaks) having longer wavelength transitions is reflected in our spectra shown in Figure 3. The higher mass samples at 5 and 13 mm have longer wavelength absorbance peaks for both the filmy-QCC as a solid and dissolved in cyclohexane.

2.4. PL of the Filmy-QCC as a Solid and Dissolved in Cyclohexane

We measured the PL spectra of the filmy-QCC with a method similar to that of Sakata et al. (1992), and this is shown in Figure 4. The filmy-QCC samples were easily oxidized in
Figure 3. (a) Absorbance spectra of the filmy-QCC, where the absorbance is the quantity $-\log_{10}(\text{transmitted light/incident light})$. The filmy-QCC was collected on a quartz glass substrate with a length of 40 mm. Spectra were measured using an aperture of 3 mm in diameter at a point along the substrate at 5 mm (solid line), 13 mm (long dash), 20 mm (short dash), and 27 mm (dot dash) from the edge adjacent to the nozzle of the apparatus. These distances correspond to the distance from the nozzle when the QCC was made. (b) Absorbance spectra of the filmy-QCC dissolved in cyclohexane. Samples were collected on four pieces of quartz glass substrates with a length of 10 mm, which were set at the distance of 5 mm (solid), 15 mm (long dash), 25 mm (short dash), and 35 mm (dot dash) from the nozzle of the apparatus. The filmy-QCC condensate on the substrates were then dissolved in cyclohexane.

Figure 4. PL spectra of the filmy-QCC excited by 365 nm line of the Hg lamp. Samples were collected at 5 mm (black), 13 mm (red), 20 mm (blue), and 27 mm (brown) from the nozzle (as described in Figure 3a). The spectra are normalized at the peak. An emission line from the Hg lamp is marked with the * symbol.

Figure 5. PL spectra of the filmy-QCC dissolved in cyclohexane. The spectra were measured by Hitachi F-4500 fluorescence spectrometer using the “366 nm” deuterium lamp. Samples were collected at 5 mm (solid), 13 mm (long dash), 20 mm (short dash), and 27 mm (dot dash) from the nozzle (as described in Figure 3b). An emission line at 366 nm from the deuterium lamp is marked with the * symbol.

Air under irradiation of UV. Therefore, we placed them in a vacuum cell and irradiated them with a 365 nm Hg lamp from outside of the cell. The filmy-QCC dissolved in cyclohexane was illuminated with a 366 nm deuterium lamp, and the PL was measured with a Hitachi F-4500 fluorescence spectrometer. Dissolved oxygen gas was removed from the cyclohexane before we used it. The spectra are presented in Figure 5. The PL spectra shown in Figures 4 and 5 show the same trend of the higher mass filmy-QCC material having peaks at longer wavelengths.

2.5. Quantum Yield of the PL

A quantum yield measurement of the PL of filmy-QCC was carried out using films with known quantum yield. We made two standard films with vapor deposition in a vacuum chamber. These were $N, N'$-diphenyl-$N, N'$-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD, quantum yield = 0.35) and $N, N'$-diphenyl-$N, N'$-bis(1-naphthylphenyl)-1,1'-biphenyl-4, 4'-diamine (NPD, quantum yield = 0.41) (Mattoussi et al. 1999).

In the case of the filmy-QCC in solution, the quantum yield was obtained by comparison to a standard solution of 9,10-Diphenylanthracene.

The quantum yield of PL is the ratio of the number of luminescence photons to that of the number of photons absorbed, $n(\text{PL})/n(\text{absorbed})$. The luminescence of neutral PAHs is caused by the electronic transition from the first electronic excitation level $S_1$ to the ground state $S_0$ ($S_0 \leftarrow S_1$). Luminescence from the second ($S_2$) or third ($S_3$) electronic excited level directly is very rare. When an electron in the molecule is excited to the level $S_2$, the electron loses energy...
through vibrational transitions to the first excited energy level \( S_1 \) (internal conversion). The electron then emits PL through the vibrational states of the first excited energy level. The distance from the nozzle of the plasma chamber.

Quantum yields were obtained by comparison to two kinds of standard films: TPD and NPD.

We list the quantum yields of the filmy-QCCs in Table 1. They are in the range of 0.009–0.04. Quantum yields obtained by the TPD as a standard film are a little smaller than those obtained by the NPD standard. For these measurements, we set up the samples and standard films in the same way. The surface roughness of the films, stray light from the substrate and quartz container, and differences of refractive indices between samples and standard films all have an effect on the measurements. Therefore, we think that the quantum yields of the QCC-films have an accuracy of only one significant figure.

Smith & Witt (2002) estimated the PL efficiency (quantum yield) in various types of astrophysical sources, and they found that it is in the range of 0.1–10%. Thus the quantum yield of filmy-QCC is within the observed range. Generally, small PAH molecules have a higher quantum yield than large PAH molecules because they have less vibrational modes for nonradiative processes. Thus the quantum yield of the filmy-QCC containing large PAHs is expected to be lower than those containing smaller PAHs. However, we could not see a clear trend of the quantum yield in the various filmy-QCCs with different PAH mass distributions. In addition, we would expect the quantum yield of small, isolated filmy-QCC particles in space to be higher than what we measure since the laboratory samples have nonradiative modes for losing energy.

Ledoux et al. (2001) reported that the quantum yield of crystalline silicon nanoparticles ranges from 0.0025 to 0.18. After correction, they obtained a quantum yield of 0.01–1 for silicon nanoparticles with sizes of 2.8–4.8 nm in diameter. They also showed that quantum yields of HAC (a-C:H) were in the range 1–9 \( \times 10^{-5} \). The quantum yields of the filmy-QCC shown in Table 1 are in the range measured for Si nanoparticles.

The quantum yields of the filmy-QCC in the cyclohexane solution are 0.12–0.16 (Table 2). As expected, this is higher than those of the filmy-QCC in the solid state (Table 1) since in the solid form the energy is transferred to various adjacent molecules. This increases the probability of energy loss through nonradiative processes, thus decreasing the PL yield.

The dark-QCC is another product from the plasmic gas. The material is a carbonaceous material with an onion-like structure. It shows a 220 nm absorption peak (Sakata et al. 1994; Wada et al. 1999) and some IEF bands. The material does not emit luminescence, although a small amount of PAHs is contained in it as shown in Figure 1. It is likely that PAHs that absorb UV photons in dark-QCC transfer energy to a large carbon network within the dark-QCC. Then the carbon network loses energy through various vibrational states and this quenches the PL in the dark-QCC.

### 2.6. Excitation Wavelength and the PL Intensity

In our PL experiment, we used monochromatic light for excitation. If the filmy-QCC is irradiated by UV photons of shorter wavelength, it will be excited to higher electronic energy levels than \( S_1 \). This means that the filmy-QCC will show some absorption features in the UV region. As discussed in Section 2.5, the quantum yield of a PAH excited to various excitation levels is approximately the same. Since the total number of PL photons emitted from a PAH is equal to the product of the quantum yield and the sum of the number of absorbed photons, both the quantum yield and the absorption spectrum are important to determine the PL intensity.

Filmy-QCC is a mixture of various types of PAHs and may also contain other types of organic molecules. Some molecules in the filmy-QCC may absorb UV photons but not produce PL. In addition, molecular interaction may be present in the filmy-QCC. A PAH may interact with a neighboring molecule differently, depending on what its excitation state is. For this reason, the absorption spectra will differ from the excitation spectra when there is a mixture of different molecules, although the excitation spectra are often similar when there is only a single molecule present. Other processes such as photoionization or photodissociation may occur at higher energy levels. Therefore, to study the PL of filmy-QCC precisely, measurements at various excitation wavelengths will be needed.

### 3. IMPLICATIONS FOR THE ERE AND BL IN THE RR

#### 3.1. Observational Characteristics of ERE and BL in the RR Nebula

The ERE is caused by the absorption of UV photons (Witt & Vjih 2004; Smith & Witt 2002). Darbon et al. (1999) found that the ERE is observed in sources where the \( T_{\text{eff}} \) of the illuminating star is \( > 10^4 \) K, and they showed that illuminating stars with \( T_{\text{eff}} < 7000 \) K do not produce the ERE. Therefore, Witt et al. (2006) suggest that the ERE is caused by the absorption of far-UV photons with wavelengths shorter than 170 nm. However, UV photons with longer wavelengths are sufficient for the excitation of PL observed in the optical region. In view of these facts, Witt et al. (2006) proposed a two-step process for ERE emission. In the first step, irradiation of far-UV photons with \( E > 10.5 \) eV creates the ERE carrier, most likely through photoionization or photodissociation of an existing precursor.
In the second step, the excitation of the ERE carrier occurs with near-UV/optical photons.

The RR is an important object since the nebular emission has high surface brightness and various types of emission spectra can be observed. Recent observations include Men’shchikov et al. (2002), Cohen et al. (2004), Sharp et al. (2006), Vĳh et al. (2005a), Vĳh et al. (2006), and Miyata et al. (2004). At the center of the RR is a binary system composed of a post-asymptotic giant branch (post-AGB) star with effective temperature about 7750 K and a helium white dwarf with a temperature of about 60,000 K (Men’shchikov et al. 2002). These stars are hidden by a thick dust torus, and the mass loss of the post-AGB star formed the present RR nebula.

The bipolar outflow from the binary system produces the X-shaped spikes in the nebula. The hot white dwarf star produces an H ii region very close to the star, but it is not bright enough to be observed directly. The star illuminates dust grains in the biconical outflow cavity. Most of the nebular mass is in the large dust grains (size ≲ 0.2 cm), which are in a dense circumbinary torus (Men’shchikov et al. 2002; Jura et al. 1997). Men’shchikov et al. (2002) suggested that small amorphous carbon grains would be present outside of the torus and in the outflow regions. Miyata et al. (2004) reported that the 8.6 and 11.2 μm bands are observed very close to the binary system, implying that the carbon-rich dust formation occurs near the central region of the torus.

The ERE is clearly observed on the wall of the biconical outflow structure. In addition, the ladder structure of the RR was also clearly observed with a red filter (Cohen et al. 2004). If the red color of the ladder is caused by ERE, the carriers formed before the recent violent outflow event. Cohen et al. (2004) reported that the mass loss started about 14,000 yr ago and the outbursts are becoming more frequent.

The peak wavelength of the ERE was observed at the different locations in the RR nebula. Witt & Boroson (1990) found that the peak wavelength varies from ~670 nm at 6° south of the star to ~645 nm at 10° south. Ledoux et al. (2001), citing the work of Rouan et al. (1995), gave a peak wavelength of ~755 nm at 2° south of the star and ~700 nm at 5°. As noted previously, the FWHM of the ERE peaks is broader as the wavelength of the peak increases. This suggests that the chemical composition, dust structure (arrangement of the molecules), dust size, and physical condition (charge) of the ERE carrier material changes with distance from the central star.

The BL spectrum shows some spectral structure and variability from location to location (Vĳh et al. 2005a), and it is slightly elongated in the east and west directions (Vĳh et al. 2006). The intensity of the ERE is very strong at the wall of the bipolar outflow, but the BL is distributed around the central region, and the BL and the ERE are not spatially correlated (Vĳh et al. 2006). Vĳh et al. (2005a) showed that there is a close spatial correlation of the 3.3 μm IEF with the BL. They suggest that the BL originates from small neutral aromatic hydrocarbon molecules.

### 3.2. Comparison of ERE and the PL of the Filmy-QCC

Although individual PAHs in the cyclohexane solution show blue–green PL, the mixture in filmy-QCC as a solid shows a red PL at longer wavelengths. This suggests that there is a strong interaction between excited PAHs with neighboring molecules in the solid filmy-QCC material. In our experiments, the PL peak of the filmy-QCCs ranged from 650 to 690 nm with a FWHM of 133–143 nm. From the mass analysis, the peak shift from 650 to 690 nm corresponds to the growth of PAH molecules in the filmy-QCC from 276 to 398 amu at the center mass of the distribution.

We show in Figure 6 the ERE spectrum 6° south of the RR (black line) from Witt & Boroson (1990) and the PL of the filmy-QCC collected at 27 mm from the nozzle (grey; see Figure 4). An emission line from the Hg lamp is marked with the * symbol.

![Figure 6. Comparison of the ERE spectrum 6° south of the RR (black line) from Witt & Boroson (1990) and the PL of the filmy-QCC collected at 27 mm from the nozzle (grey; see Figure 4). An emission line from the Hg lamp is marked with the * symbol.](image)

The PL peak wavelength of the filmy-QCC depends weakly on the size of molecules. Sakata et al. (1992) formed the filmy-QCCs on substrates at a given location with different temperatures. They showed that the PL peak of the sample formed on the higher temperature substrate occurs at longer wavelengths. Thus the temperature of the substrate is an important factor for growth of PAH molecules. In their experiments, the filmy-QCCs show a peak ranging from 650 to 725 nm.

We did not find variations of the PL bandwidth of the filmy-QCC. All filmy-QCCs have a similar FWHM. Since the FWHM depends on the mass distribution of PAHs, we think that the right size distribution of PAHs is necessary for good matching to the width of the ERE band observed in the RR.

### 3.3. Comparison of BL and PL of the Filmy-QCC Solution

The BL spectrum of the RR (Vĳh et al. 2004) and a PL spectrum of the filmy-QCC solution collected at 35 mm from the nozzle (center mass peak about 256 amu) are compared with the BL spectra of the RR (Figure 7). The PL of the filmy-QCC solution is at shorter wavelengths than the filmy-QCC; however, the observed peak of BL is at an even shorter wavelength. This suggests that BL carriers are smaller PAHs than emitters in the filmy-QCC, and this agrees with Vĳh et al. (2005a), who estimate that the BL emitters have approximately three or four rings.
The pressures are very low compared to those in Section 2.2. These molecules have first ionization energy of about 7 eV for anthracene and coronene of filmy-QCC, we calculated the vapor pressure between its components.

The dust grains showing ERE in the RR nebula should also be a mixture of various PAHs. We can approximate their vapor pressures using the data of pure crystals. Assuming 360 K for the dust temperature and 300 K for the substrate temperature of the filmy-QCC synthesis, we calculated the vapor pressure of pure anthracene to be $7.0 \times 10^{-3}$ and $8.4 \times 10^{-6}$ Torr, respectively, using the data of Oja & Suuberg (1997). Similarly, the vapor pressures of pure coronene (300 amu) are obtained about $4.7 \times 10^{-9}$ and $4.7 \times 10^{-12}$ Torr, respectively, from data of Zacharia et al. (2004). The pressures are very low compared to those of anthracene, since the vapor pressure of PAHs decreases rapidly with increasing molecular size. We therefore think it is reasonable that small PAHs are present in the gas phase and large PAHs are condensed on dust grains.

### 3.4. Ionization State of the ERE Carrier

Since PAH molecules have a low ionization potential, we expect that they would be ionized in the biconical outflow cavities of the RR. We found that the PAH molecules in the filmy-QCC have a mass of about 200–500 amu as discussed in Section 2.2. These molecules have first ionization energy ranging from 8 eV (155 nm) to 6 eV (207 nm) and the second ionization potential of 13 eV (95 nm) to 11 eV (113 nm) (Witt et al. 2006). Cations that are excited usually do not emit PL, since the energy of an excited cation is lost quickly by nonradiative processes. However, Witt et al. (2006) suggested that dications of PAHs are possible ERE carriers. In support of this, Rhee et al. (2007) reported that closed-shell dications and closed-shell PAH dimers can emit PL. If carriers of the ERE are dications of isolated PAH molecules, then we could detect discrete emission peaks in the ERE spectrum. Indeed, some sharp peaks are seen overlaid on the broad ERE feature spectra of the RR. The carriers of the sharp peaks are thought to be isolated molecular species. However, the underlying broad ERE feature is well explained by dust grains.

In general, condensed PAHs possess lower ionization energy than the PAHs in the gaseous state because of the electronic polarization induced by the surrounding molecules. For example, the work function of pentacene is 5.15 eV (Fukagawa et al. 2006), and the ionization energy of pentacene molecule is 6.74 eV (Boschi et al. 1974). In comparison, we obtained 5.3 eV for the work function of the filmy-QCC by UV photoelectron spectroscopy with He I. This corresponds to the energy of a photon with a wavelength of 234 nm.

The charge number of the dust grains in a radiation field depends on various factors, such as the threshold energy of photoionization, photoelectron emission yield, energy distribution of radiation field, etc. Weingartner et al. (2006) estimated the threshold energy of the photoelectric emission from dust grains. From their Figure 4 we can see that that the ionization of small dust grains begins with photon energies greater than $\sim 6$ eV, slightly higher than that required to ionize the filmy-QCC material. Abbas et al. (2006) measured the yield of photoelectric emission of astronomical dust candidates experimentally. They showed that the yield also depends on the wavelength of the photon and the particle size of grains. The photoelectron emission yield of carbonaceous grains with a radius of about 400 nm is about $10^{-3}$ at the wavelength of 160 nm and $10^{-4}$ at 140 nm and the yield increases with the size of particles. Thus, based on the calculations of Weingartner et al. (2006) and the low photoelectron emission yield of Abbas et al. (2006), we believe it is reasonable that dust particles in the outflow cavities of the RR are at least partially ionized and contain both neutral PAH molecules and some charged PAH ions. The neutral PAH molecules in the dust particles could emit red PL under irradiation by UV photons, as is observed in the outflow cavities of the RR.

Witt et al. (2006) suggested that photons with energy greater than $10.5$ eV are necessary for the formation of the ERE carrier from the study of NGC 7023. If this is true in the RR, then we think that neutral PAHs may be formed photochemically. PAHs are often formed from simple species such as CH, C$_2$, etc., in plasma processes, and in combustion processes of organic molecules. Such simple species are expected to form by photolysis of saturated organic molecules, and PAHs and their particles will be formed from them.

### 3.5. ERE and IEF Carriers—Decomposition of Dust Particles by UV Irradiation

Kerr et al. (1999) reported that the distribution of 3.3 $\mu$m IEF in RR does not correlate to the ERE distribution. Instead, the distribution of 3 $\mu$m band correlates to the BL distribution (Vijh et al. 2005a). The filmy-QCC shows infrared absorption bands in the 3 $\mu$m region as shown in previous papers (Sakata et al. 1990; Wada et al. 2003). Why does the ERE carrier not emit the 3.3 $\mu$m band but emit ERE? Draine & Li (2001) reported that only particles with very small size are heated by UV absorption and emit at near-infrared wavelengths. It is probable that the ERE emitter is too cold to emit in the 3.3 $\mu$m band after the absorption of UV photon because the emitter is a cluster of PAHs.
Under irradiation by hard UV photons, ERE dust grains will gradually decompose because of (1) heating by the UV photons and (2) electrostatic disruption of dust grains due to a high degree of ionization as discussed by Waxman & Draine (2000). Since dust grains are a material coagulated with Van der Waals forces, the electrostatic disruption of the dust will occur easily. As a result, the ERE dust grains cannot survive for long under irradiation by hard UV photons. Because of the decomposition of the dust grains, isolated PAH molecules and ions are supplied in the outflow cavities. 

Vuong & Foing (2000) discussed the dehydrogenation of PAH molecules after the absorption of UV photons. The dissociation energy of the C–H bond of PAH cations is about 4 eV. They showed that PAHs with less than 40 carbon atoms are completely or strongly dehydrogenated. However, PAHs with more than 40 carbon atoms are very stable against dehydrogenation. Le Page et al. (2003) estimated the states of charge and hydrogenation of PAH molecules under UV irradiation. They reported that dehydrogenated PAHs, \( C_m H_n \) and \( C_m H_n^{(+)} \), where \( m \) is from 15 to 30 and \( n < 2 \) can survive. Therefore, isolated PAH molecules and ions supplied by dusts will lose most of their hydrogen atoms. The resulting products with a few hydrogen atoms are not exactly PAHs as defined in chemistry, although their skeletal structure is similar to PAHs. From this viewpoint they can be considered to be fragments of soot. These products can emit infrared bands when they are heated stochastically, and they could be the IEF carriers. In this scenario, we suspect that the ERE carriers give rise to the IEF carriers through a process of decomposition and dehydrogenation.

Recently, Berné et al. (2008) reported that the ERE emission region in NGC 7023 is different from that of IEF bands which is caused by ionized IEF carriers. But their result indicates that the ERE arises from the region where neutral IEF carriers are abundant. They suggested the ERE carrier is a transition species, such as the dimer \( [PAH_2]^+ \) formed during the destruction of very small carbonaceous grains and not the doubly ionized PAH molecules as suggested by Witt et al. (2006).

Can the QCC model explain this observation? The correlation between the ERE to IEF caused by neutral IEF carriers also prefers a neutral ERE candidate, such as QCC, to PAH dication. The correlation of ERE and IEF can also be explained by a hypothesis that the IEF carriers are supplied by evaporation of the ERE carrier. However, the formation mechanism of the ERE carrier is still not clearly understood. Further study will be needed.

### 3.6. UV Extinction

Vijh et al. (2005a) discuss the extinction curve of the RR, which is strongly affected by dust near the central binary and is very different from the Galactic interstellar extinction curve. The 217.5 nm absorption feature was not observed, and a strong extinction increase is observed at wavelengths shorter than 167 nm. Vijh et al. (2005a) attribute this increase to the onset of ionization of PAHs with masses less than 250 amu. They also attribute the broad UV extinction feature at 3–5 \( \mu m \) to absorption by small PAHs with a continuum of sizes and an ionization potential \( > 7.4 \) eV.

Carriers of ERE and BL and other dusts (for example, silicates) in the central region of RR contribute to the extinction curve. Sharp strong absorption peaks are not observed in the extinction curve, and so candidates for the carrier must possess broad absorption peaks. If a candidate possesses sharp absorption features, then the abundance must be very low. As a general rule, the sharpness of an absorption feature of a PAH decreases for a gas, a solution, and a solid in this order. In addition, a solid formed from PAH mixtures show broader features than a pure PAH solid.

Absorption spectra of the filmy-QCCs and in solvents give clues to the contribution of PAH molecules to the extinction curve. Filmy-QCCs collected at various locations from the nozzle show different absorption spectra. The absorption bands range from the visible to UV. The absorption spectra have two or three bands in the wavelength range of 200–530 nm. Mixtures of filmy-QCCs can produce a broad bump around 3–5 \( \mu m \) (200–330 nm). Gaseous anthracene might be one of the carriers for BL, and shows a sharp absorption feature about 4.2 \( \mu m \) (Joblin et al. 1992). However, this peak is not seen in the extinction spectrum. This means that the abundance of anthracene is low although it emits PL at high efficiency at the BL wavelengths. Quantitative analysis is necessary to constrain possible PAH carriers for the BL.

### 4. CONCLUSIONS

We obtained the following experimental results about the properties of filmy-QCC.

1. The major components of the filmy-QCC are PAHs. The sizes were found to be 200–500 amu.
2. The filmy-QCC shows red PL with a peak wavelength ranging from 650 to 690 nm with a FWHM of 133–143 nm. Our experiments suggest that the PAHs are major emitters of the PL. The PL quantum yield of our filmy-QCC samples ranges from 0.009 to 0.04.
3. A solution of the filmy-QCC dissolved in cyclohexane shows PL at 400–500 nm with a quantum yield of 0.12–0.16. The large difference in the wavelength of the PL peak between the coagulated PAH molecules in filmy-QCC and the dispersed PAH molecules in a solution indicates a strong intermolecular interaction of the PAH with neighboring molecules in the filmy-QCC.

Witt & Vijh (2004) summarized the observational constraints on any proposed carrier for the ERE. The high quantum yield of filmy-QCC as a solid makes filmy-QCC a viable candidate as the carrier of the ERE. While not as high as the maximum PL efficiency (quantum yield) found by Smith & Witt (2002), filmy-QCC does show a quantum yield that is similar to what is observed in many astrophysical sources. One can expect that the quantum yield of small, isolated particles of filmy-QCC would be higher than what is measured under laboratory conditions.

Filmy-QCC also fits other constraints listed by Witt & Vijh (2004): it is composed of cosmically abundant elements, and it can plausibly survive under a wide range of interstellar and circumstellar environments since it is composed of PAH molecules. No PL is emitted by filmy-QCC at 350–500 nm with UV excitation; and the PL occurs in the correct wavelength range. However, our experiments thus far have not demonstrated other constraints that include a strong correlation of the width and peak wavelength of the ERE emission and a correlation of the peak wavelength and quantum yield on the density and hardness of the UV photons. These correlations depend on the particle size of the emitter, and we are not able to synthesize filmy-QCC particles in the size range that exists in the interstellar medium.

The PL of filmy-QCC dissolved in cyclohexane shows that it likely arises from small PAH molecules that are present in
the filmy-QCC. The PL spectra overlaps with the spectra of BL, and this supports the idea suggested by Vijh et al. (2005a) that small PAH molecules in the gas phase are possible BL carriers.

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