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Mixed aromatic–aliphatic organic nanoparticles as carriers of unidentified infrared emission features

Sun Kwok[1] & Yong Zhang[1]

Unidentified infrared emission bands at wavelengths of 3–20 micrometres are widely observed in a range of environments in our Galaxy and in others[1]. Some features have been identified as the stretching and bending modes of aromatic compounds[2,3], and are commonly attributed to polycyclic aromatic hydrocarbon molecules[4,5]. The central argument supporting this attribution is that single-photon excitation of the molecule can account for the unidentified infrared emission features observed in 'cirrus' clouds in the diffuse interstellar medium[6]. Of the more than 160 molecules identified in the circumstellar and interstellar environments, however, not one is a polycyclic aromatic hydrocarbon molecule. The detections of discrete and broad aliphatic spectral features suggest that the carrier of the unidentified infrared emission features cannot be a pure aromatic compound. Here we report an analysis of archival spectroscopic observations and demonstrate that the data are most consistent with the carriers being amorphous organic solids with a mixed aromatic–aliphatic structure. This structure is similar to that of the organic materials found in meteorites, as would be expected if the Solar System had inherited these organic materials from interstellar sources.

For the past 20 years, polycyclic aromatic hydrocarbon (PAH) molecules have commonly been considered the carriers of unidentified infrared emission (UIE) features. This hypothesis assumes that the UIE features are the result of infrared fluorescence from small (~50-carbon-atom) gas-phase PAH molecules being pumped by far-ultraviolet photons[7]. In spite of its popularity, the PAH hypothesis does not provide

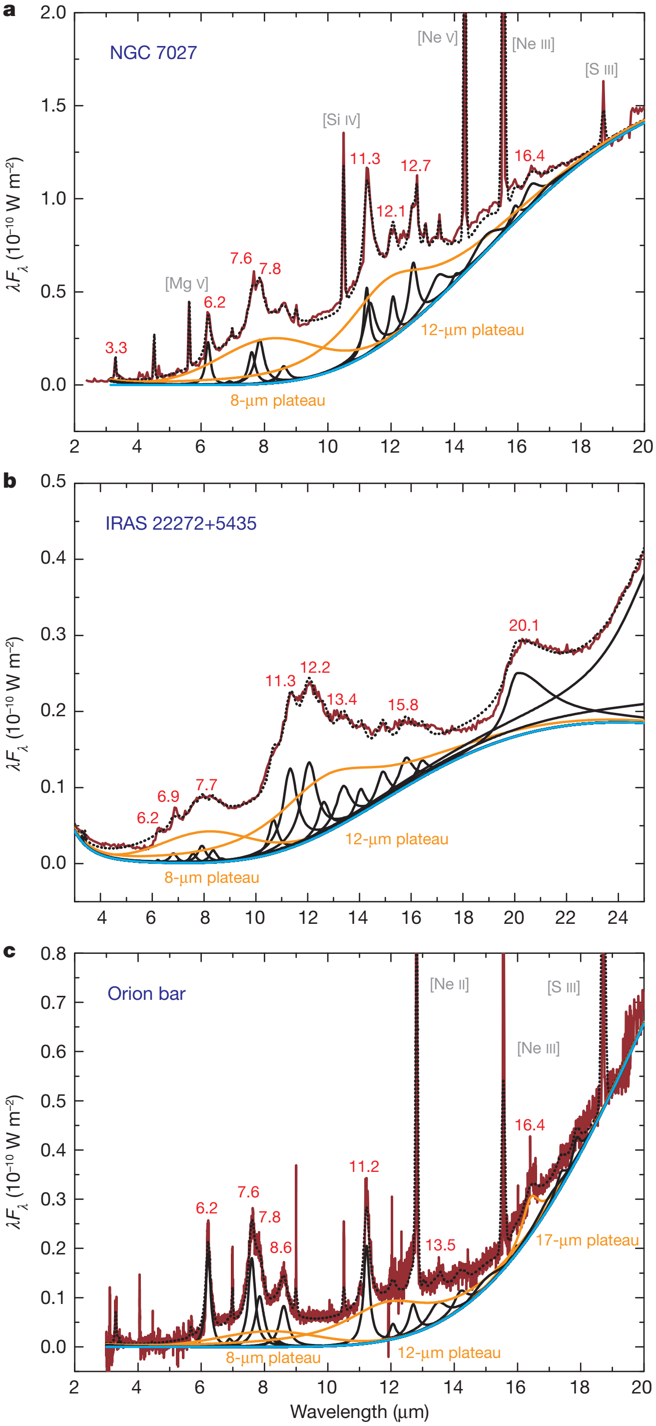

Figure 1 | Mixed aromatic and aliphatic features in the infrared spectra of circumstellar and interstellar nebulae. a–c, Spectral decompositions of the UIE features of the planetary nebula NGC 7027 (**a**), the proto-planetary nebula IRAS 22272+5435 (**b**) and the Orion bar photodissociation region (**c**), showing a mix of aromatic, aliphatic and continuum features. The observed flux at wavelength λ, F_λ, is proportional to the emission intensity at that wavelength. A series of discrete features (black lines) and plateau features (orange lines; in **c**, the 17-µm plateau represents the 15–20-µm range) superposed on a continuum (blue line) have been fitted to the observed data. The UIE and plateau features (wavelengths in micrometres), as well as some of the atomic lines, are marked. The observed spectra are shown as solid red lines and the fitted spectra are shown as dotted black lines. The origin of the 20.1-µm feature in the IRAS 22272+5435 spectrum is currently unidentified. The spectral data for NGC 7027, IRAS 22272+5435 and the Orion bar are retrieved from the Infrared Space Observatory archive. For the spectral decomposition, we used the IDL package PAHFIT originally developed to fit the Spitzer Space Telescope Infrared Spectrograph spectra of nearby galaxies. The model spectra take into account the contributions from the stellar continuum, the thermal dust continuum, H_2 emission, atomic emission lines, the UIE features (both aromatic and aliphatic) and the plateau emission features. The optimal fitting to the observed spectra is achieved through the Levenberg–Marquardt least-squares algorithm. A modified blackbody model for the emission intensity at wavelength λ, $I_\lambda \propto \lambda^{-\alpha} B_\lambda(T)$, where $B_\lambda(T)$ is the blackbody function with a temperature T, is used to fit the continuum. The aromatic, aliphatic and plateau features are fitted with assumed Drude profiles $I_\lambda \propto \gamma^2[(\lambda/\lambda_0 - \lambda_0/\lambda)^2 + \gamma^2]^{-1}$, where λ_0 is the central wavelength and γ is the fractional full-width at half-maximum of each feature.

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[1] Department of Physics, Faculty of Science, The University of Hong Kong, Pokfulam Road, Hong Kong, China.

a good explanation for the observed spectral behaviour. PAH molecules are fused ring molecules made up of carbon and hydrogen, and their vibrational bands are sharp and the peak wavelengths well defined. To fit the broad profiles of the UIE features seen in astronomical spectra, it is necessary to use a complex mixture of PAHs of different sizes, structures and charge states, and to utilize empirical feature profiles[8,9]. Because PAH molecules require ultraviolet photons to excite them, they cannot explain the presence of UIE features in reflection nebulae[10] and proto-planetary nebulae[11] where the central stars are cool and there is no ultraviolet background radiation. To account for these facts, the PAH model has to be revised to include large clusters and other ionization states.

The central argument for the PAH hypothesis is that single-photon excitation of PAH molecules can account for the 12-μm excess emission observed in cirrus clouds in the diffuse interstellar medium by the Infrared Astronomical Satellite (IRAS). However, the UIE-band flux ratios in the diffuse H II regions in the Carina nebula are nearly constant over a range of three orders of magnitude in background radiation[12]. The shapes and peak wavelengths of the UIE features are independent of the temperature of the central stars providing the excitation[10]. Furthermore, PAH molecules have strong and narrow absorption features in the ultraviolet, but these are not observed in interstellar extinction curves[13]. However, the 3.4-μm aliphatic carbon–hydrogen stretching mode is commonly observed in absorption in the diffuse interstellar medium[14]. Although their rotational and vibrational frequencies are well known, not a single PAH molecule has yet been identified in space[15].

Other arguments have been made to support the PAH hypothesis: the asymmetric profiles of the UIE features can be explained by anharmonicity associated with molecular emission, and the observed feature-to-continuum ratio is high and therefore implies that the carrier is a molecule[7]. Laboratory spectra of mixed aromatic and aliphatic solid materials have asymmetric profiles[16], which can more naturally explain the observations. Although the observed feature-to-continuum ratio is high in the diffuse interstellar medium, it is not high in the spectra of planetary and proto-planetary nebulae. Even in the diffuse interstellar medium, the strength of the UIE features are strongly correlated with the dust continuum, suggesting a possible physical relationship between the two components[17].

The basic premise of the PAH hypothesis does not concern the chemical composition of the carrier so much as its size. As long as the carrier is a nanoparticle that can undergo transient heating, it will satisfy the excitation requirement. Laboratory experiments have yielded carbon nanoparticles with structures of sp^2 rings connected by networks of aliphatic chains[18,19], as well as fullerene fragments linked by aliphatic groups[20]. These nanoparticles are likely to be constituents in circumstellar and interstellar environments. Furthermore, it has been proposed that the possible sudden release of chemical energy as a source of transient heating of small grains will allow much larger particles to radiate in the near-infrared, further weakening the PAH hypothesis[21].

An alternative explanation to the UIE bands is that they are emitted by complex organic solids with disorganized structures. These solids intrinsically have broad emission profiles, and the features often sit on even broader emission plateaux several micrometres in width. It has been argued for some time that the observed spectral properties of UIE bands resemble those of coal and kerogen[22,23]. Coal and kerogen are amorphous organic solids with a mixed sp^2–sp^3 composition with randomly oriented aromatic ring units linked by long, aliphatic chains. Their mixed sp^2–sp^3 chemistry gives rise to the discrete aromatic and aliphatic emission features and the broad plateau features[16].

To provide a quantitative comparison between the two models, we have performed spectral decomposition of several sources with strong UIE features. Figure 1 shows a fit to the infrared spectra of the planetary nebula NGC 7027, the proto-planetary nebula IRAS 22272+5435 and

Table 1 | Strengths of the UIE discrete and plateau features

	Discrete features* (%)									
	Aromatic					Aliphatic		Unknown		
λ (μm)	3.3	6.2	7.7	8.6	11.3	3.4	6.9	15.8	16.4	18.9
NGC 7027	0.32	1.2	2.8	0.58	3.1	0.07	0.11	0.31	0.84	0.0
IRAS 22272+5435†	0.08	0.05	0.30	0.11	3.76	0.15	0.43	0.94	0.41	—
Orion bar	0.67	3.8	7.0	2.2	2.6	0.13	0.37	0.24	2.0	0.0
V2361 Cygni	0.27‡	0.87§	0.60‖	0.03	—	—	0.25	—	—	—
V2362 Cygni	—	5.2	2.4	0.8	—	—	3.2	—	—	—

	Plateau features (%)			
	Aromatic	Aliphatic		Unknown
λ (μm)		8	12	17
NGC 7027		18.8	17.2	0.33
IRAS 22272+5435		12.5	18.6	—
Orion bar		9.3	15.1	0.78
V2361 Cygni		11.1	1.3	—
V2362 Cygni		17.1	1.2	1.1

	Continuum			Total flux (3-20 μm) (W m^{-2})
	Percentage of total flux	Temperature (K)	α	
NGC 7027	50.7	100	2	8.9 (−11)
IRAS 22272+5435	40.8	100	2	2.5 (−11)
Orion bar	47.3	70	2	2.4 (−11)
V2361 Cygni	84.8	350	0.2	1.8 (−13)
V2362 Cygni	66.8	365	0.5	2.1 (−13)

The UIE phenomenon is complex. In addition to the commonly observed 3.3-, 6.2-, 7.7-, 8.6- and 11.3-μm aromatic features, there are also aliphatic features at 3.4 and 6.9 μm, arising respectively from symmetric and asymmetric carbon–hydrogen stretching and bending modes of methyl and methylene groups attached to aromatic rings. Features at 15.8, 16.4, 17.4 (not shown), 17.8 (not shown), and 18.9 μm have been found in proto-planetary nebulae[11], reflection nebulae[30] and galaxies. In addition to the discrete features, broad emission features up to several micrometres in width are also seen. The 8- and 12-μm plateau features and a broad feature covering the 15–20-μm range (represented by 17 μm in the table) have been detected in young stellar objects, compact H II regions and planetary nebulae. The 8- and 12-μm plateaux are broad emission features (full-width at half-maximum, 2–4 μm) and can be identified as collective in-plane and, respectively, out-of-plane bending modes of a mixture of aliphatic side groups attached to aromatic rings[27]. The 15–20-μm plateau feature is also found to be strong in some proto-planetary nebulae. This table summarizes the relative contributions of these components of the spectra shown in Figs 1 and 3.

* The total fluxes and percentages refer to the values emitted in the 3–20 μm range for NGC 7027 and Orion bar, 5–20 μm for V2362 Cygni and V2361 Cygni, and 3–25 μm for IRAS 22272+5435.

† For IRAS 22272+5435, there are additional features that contribute to the flux in the 3–25-μm range. Features at 12.2, 13.4 and 20.1 μm contribute 3.83, 1.53 and 2.56%, respectively. Some of the contributions also come from the broad 26-μm feature.

‡ This entry refers to the spectral feature at 5.3 μm.

§ This entry refers to the spectral feature at 6.3 μm.

‖ This entry refers to the spectral feature at 7.2 μm.

the Orion bar, a photodissociation region in the Orion nebula, using a set of discrete UIE features, broad plateau features, and the underlying dust continuum. The breakdown of contributions to the total fluxes from various components is summarized in Table 1. The strongest component is the continuum, which contributes approximately half of the total fluxes emitted in the 3–20-μm region. The next strongest are the plateau features, which account for 36, 31 and 25% of the total fluxes from NGC 7027, IRAS 22272+5435 and the Orion bar, respectively, compared with the totals of 8, 4 and 16% from the aromatic features. The aliphatic branches probably constitute a significant fraction of the material in each of the three sources.

The above fitting results show that the carrier of the UIE features includes a mixture of aromatic and aliphatic components, and is not a pure or predominantly aromatic compound. Because the carrier is formed from a mixture of cosmic gases, it is likely that the compound will include other abundant elements such as oxygen, nitrogen, sulphur and so on, in addition to carbon and hydrogen. These impurities may also have spectral signatures that can be identified by observations at higher spectral resolution. A sketch of the proposed chemical structure is shown in Fig. 2.

The best way to study the origin of the UIE features is to observe them when they are formed. From observations of objects in the late stages of stellar evolution, we know that the UIE features develop in the circumstellar environment within a few hundred years after the termination of the asymptotic giant branch[24]. Spectroscopic observations of novae have shown that the 3.3- and 3.4-μm features appear soon after dust condensation[25]. Theoretically, it is difficult to understand how complex organics can form under such low-density conditions, but novae are observed to change from a pure gas spectrum to a dust-dominated spectrum over the course of days[26]. In Fig. 3, we show a fit to Spitzer spectra of the novae V2362 Cygni and V2361 Cygni. It is expected that a mixture of miscellaneous aliphatic branches will attach to the newly formed ring clusters. The prominence of the plateau features reflects this early stage of organic dust condensation[27].

We note that the dominant organic content in carbonaceous chondrites is a kerogen-like macromolecular solid referred to as insoluble organic matter. Recent laboratory analysis of the insoluble organic matter in the Murchison meteorite has suggested that it has a chemical structure very similar to that which we propose here[28,29]. The presence of insoluble organic matter in meteorites is evidence that complex organic solids form in nature with no difficulty. The fact that insoluble organic matter and circumstellar dust have similar chemical structures offers the possibility that Solar System organics may have a stellar connection.

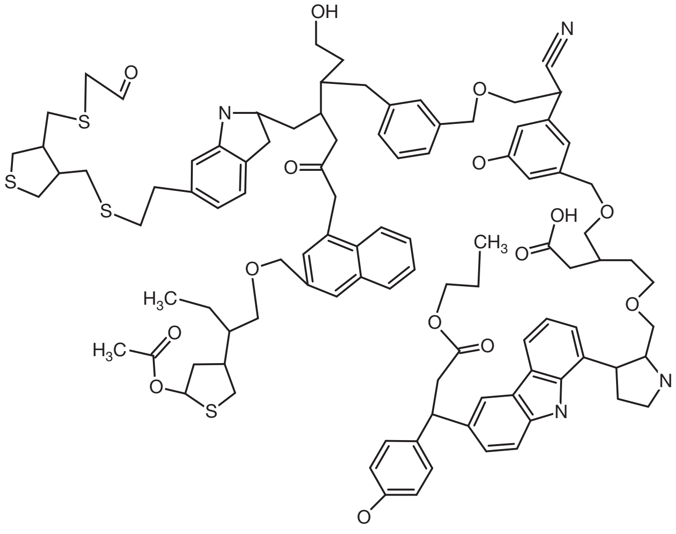

Figure 2 | Proposed structure of the carrier of UIE features. The structure is characterized by a highly disorganized arrangement of small units of aromatic rings linked by different kinds of aliphatic chain. Other impurities such as oxygen, nitrogen and sulphur are also commonly present. This structure contains about 100 carbon atoms and a typical nanoparticle may consist of multiple structures similar to this one.

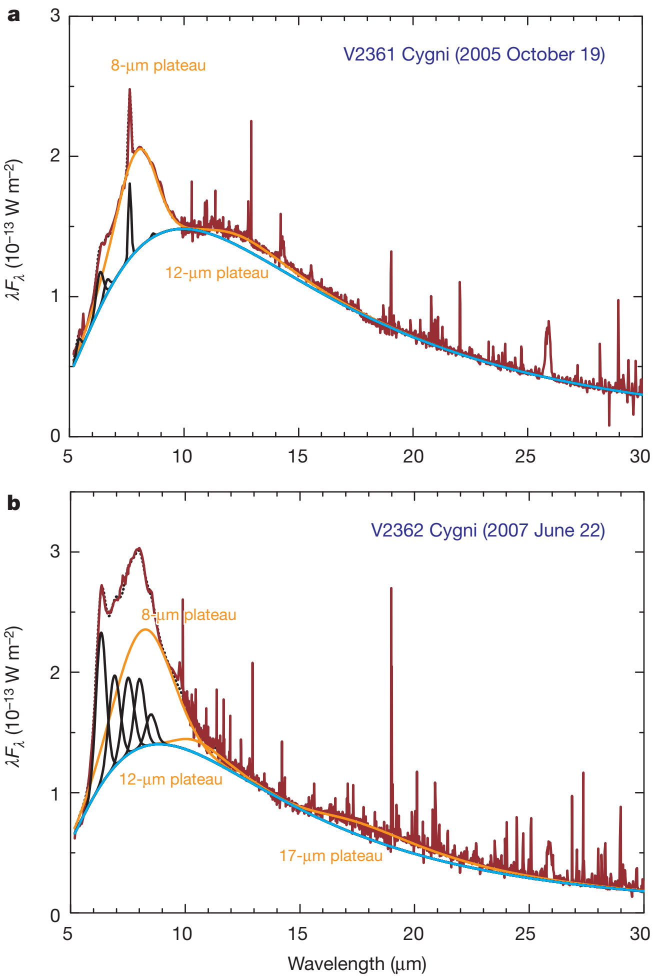

Figure 3 | Emergence of complex organics after nova outburst. a, **b**, Fits to the Spitzer Infrared Spectrograph spectra of novae V2361 Cygni (**a**) and V2362 Cygni (**b**) 251 and 446 days after their respective outbursts. In addition to the gas emission line spectrum, both spectra have developed strong dust continua, and the 8- and 12-μm plateau features are clearly present. The continua of V2361 Cygni and V2362 Cygni are fitted by modified blackbody intensities of the respective forms $\lambda^{-0.2}B_\lambda(350\,\mathrm{K})$ and $\lambda^{-0.5}B_\lambda(365\,\mathrm{K})$ (blue lines). The orange lines are the 8-, 12- and 17-μm plateau features and the solid black lines are discrete features at 5.3, 6.3, 6.9, 7.2 and 8.6 μm for V2361 Cygni and at 6.2, 6.9, 7.6, 7.8 and 8.6 μm for V2362 Cygni. The observed spectra are shown as solid red lines and the fitted spectra are shown as dotted black lines. The presence of the 8- and 12-μm plateau features suggests that the aliphatic component is the first to emerge after dust condensation. Because of the large number of emission lines, the atomic lines are not included in the fitting.

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1. Kwok, S. *Organic Matter in the Universe* (Wiley, 2011).
2. Knacke, R. F. Carbonaceous compounds in interstellar dust. *Nature* **269,** 132–134 (1977).
3. Duley, W. W. & Williams, D. A. The infrared spectrum of interstellar dust: surface functional groups on carbon. *Mon. Not. R. Astron. Soc.* **196,** 269–274 (1981).
4. Allamandola, L. J., Tielens, A. G. G. M. & Barker, J. R. Interstellar polycyclic aromatic hydrocarbons: the infrared emission bands, the excitation/emission mechanism and the astrophysical implications. *Astrophys. J. Suppl. Ser.* **71,** 733–775 (1989).
5. Puget, J. L. & Léger, A. A new component of the interstellar matter: small grains and large aromatic molecules. *Annu. Rev. Astron. Astrophys.* **27,** 161–198 (1989).

6. Sellgren, K. The near-infrared continuum emission of visual reflection nebulae. *Astrophys. J.* **277,** 623–633 (1984).
7. Tielens, A. G. G. M. Interstellar polycyclic aromatic hydrocarbon molecules. *Annu. Rev. Astron. Astrophys.* **46,** 289–337 (2008).
8. Peeters, E. *et al.* The rich 6 to 9 μm spectrum of interstellar PAHs. *Astron. Astrophys.* **390,** 1089–1113 (2002).
9. Draine, B. T. & Li, A. Infrared emission from interstellar dust. IV. The silicate-graphite-PAH model in the post-Spitzer era. *Astrophys. J.* **657,** 810–837 (2007).
10. Uchida, K. I., Sellgren, K., Werner, M. W. & Houdashelt, M. L. Infrared Space Observatory mid-infrared spectra of reflection nebulae. *Astrophys. J.* **530,** 817–833 (2000).
11. Kwok, S., Volk, K. & Hrivnak, B. J. Chemical evolution of carbonaceous materials in the last stages of stellar evolution. *Astron. Astrophys.* **350,** L35–L38 (1999).
12. Onaka, T. Interstellar dust: what do space observations tell us? *Adv. Space Res.* **25,** 2167–2176 (2000).
13. Clayton, G. C. *et al.* The role of polycyclic aromatic hydrocarbons in ultraviolet extinction. I. Probing small molecular polycyclic aromatic hydrocarbons. *Astrophys. J.* **592,** 947–952 (2003).
14. Pendleton, Y. J. & Allamandola, L. J. The organic refractory material in the diffuse interstellar medium: mid-infrared spectroscopic constraints. *Astrophys. J. Suppl. Ser.* **138,** 75–98 (2002).
15. Pilleri, P. *et al.* Search for corannulene ($C_{20}H_{10}$) in the Red Rectangle. *Mon. Not. R. Astron. Soc.* **397,** 1053–1060 (2009).
16. Guillois, O., Nenner, I., Papoular, R. & Reynaud, C. Coal models for the infrared emission spectra of proto-planetary nebulae. *Astrophys. J.* **464,** 810–817 (1996).
17. Kahanpää, J., Mattila, K., Lehtinen, K., Leinert, C. & Lemke, D. Unidentified infrared bands in the interstellar medium across the Galaxy. *Astron. Astrophys.* **405,** 999–1012 (2003).
18. Sakata, A., Wada, S., Onaka, T. & Tokunaga, A. T. Infrared spectrum of quenched carbonaceous composite (QCC). II. A new identification of the 7.7 and 8.6 micron unidentified infrared emission bands. *Astrophys. J.* **320,** L63–L67 (1987).
19. Duley, W. W. & Hu, A. Polyynes and interstellar carbon nanoparticles. *Astrophys. J.* **698,** 808–811 (2009).
20. Jäger, C., Huisken, F., Mutschke, H., Jansa, I. L. & Henning, T. H. Formation of polycyclic aromatic hydrocarbons and carbonaceous solids in gas-phase condensation experiments. *Astrophys. J.* **696,** 706–712 (2009).
21. Duley, W. W. & Williams, D. A. Excitation of the aromatic infrared emission bands: chemical energy in hydrogenated amorphous carbon particles? *Astrophys. J.* **737,** L44 (2011).
22. Papoular, R., Conrad, J., Giuliano, M., Kister, J. & Mille, G. A coal model for the carriers of the unidentified IR bands. *Astron. Astrophys.* **217,** 204–208 (1989).
23. Papoular, R. The use of kerogen data in understanding the properties and evolution of interstellar carbonaceous dust. *Astron. Astrophys.* **378,** 597–607 (2001).
24. Kwok, S. The synthesis of organic and inorganic compounds in evolved stars. *Nature* **430,** 985–991 (2004).
25. Evans, A. *et al.* Infrared spectroscopy of nova Cassiopeiae 1993. IV. A closer look at the dust. *Mon. Not. R. Astron. Soc.* **360,** 1483–1492 (2005).
26. Ney, E. P. & Hatfield, B. F. The isothermal dust condensation of Nova Vulpeculae 1976. *Astrophys. J.* **219,** L111–L115 (1978).
27. Kwok, S., Volk, K. & Bernath, P. On the origin of infrared plateau features in proto-planetary nebulae. *Astrophys. J.* **554,** L87–L90 (2001).
28. Derenne, S. & Robert, F. Model of molecular structure of the insoluble organic matter isolated from Murchison meteorite. *Meteorit. Planet. Sci.* **45,** 1461–1475 (2010).
29. Cody, G. D. *et al.* Establishing a molecular relationship between chrondritic and cometary organic solids. *Proc. Natl Acad. Sci. USA* advance online publication, ⟨http://dx.doi.org/10.1073/pnas.1015913108⟩ (4 April 2011).
30. Sellgren, K., Uchida, K. I. & Werner, M. W. The 15–20 μm Spitzer spectra of interstellar emission features in NGC 7023. *Astrophys. J.* **659,** 1338–1351 (2007).

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