# Vibrational Spectra and Molecular Organization in Thin Solid Films of 2,3-Naphthalocyanines

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The spectroscopic properties and morphology of evaporated thin solid films of metal-free 2,3-naphthalocyanine ($H_2Nc$) and the copper complex (CuNc) are reported. The vibrational spectra of the neat material and their films include: Raman (RS), resonance Raman (RRS), surface-enhanced resonance Raman scattering (SERRS), middle- and far-infrared spectra of the $H_2Nc$ and CuNc. The molecular organization of vacuum-evaporated thin films was probed by transmission and reflection—absorption FTIR spectroscopy (RAIRS). Film morphology was studied using scanning and transmission electron microscopy (SEM and TEM). Films of $H_2Nc$ and CuNc were exposed to $NO_2$, and the gas adsorption was monitored by visible absorption spectroscopy and SERRS.

## Introduction

2,3-Naphthalocyanines (Nc)[1,2] are well-known organic dyes of great interest for their potential use as organic semiconductors,[2,3] nonlinear optical materials,[4] photosensitizers,[5-8] photoelectrochemical cells,[9,10] and many others. Nc are phthalocyanine (Pc) derivatives with a larger aromatic system consisting of four benzoisoindole units (the molecular structure of $H_2Nc$ is given in Figure 1). Due to this extended π-electron-delocalized system, these materials exhibit strong absorption bands in the near-infrared region. These red-shifted electronic absorption maxima, and their photoconductive properties also make them suitable candidates for applications in solar energy conversion and laser electrophotography.[11]

The epitaxial growth of vacuum-evaporated thin films of several Nc on different substrates has been studied using transmission electron microscopy (TEM), high-resolution electron microscopy (HREM), and scanning tunneling microscopy (STM).[12-14] The influence of the
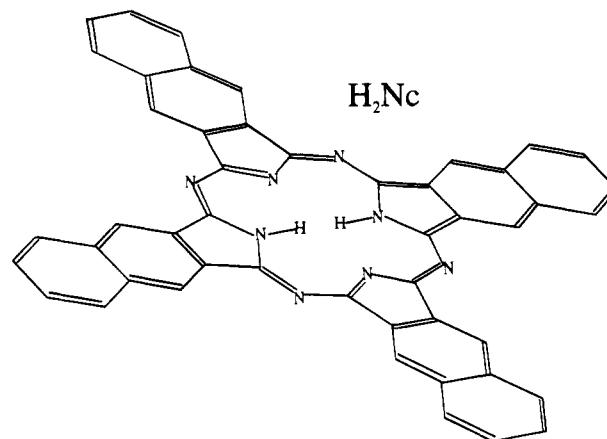


**Figure 1.** Illustration of the molecular geometry of $H_2Nc$.

substrate temperature during deposition was shown to play an important role in the crystal structure of the thin organic films. Recently, this observation has been confirmed for evaporated films of CoNc using atomic force microscopy (AFM).[15] Kaplan et al.[2] and Yanagi et al. have reported the infrared spectra of some Nc in the transmission and reflection—absorption geometries.[16,17] Different molecular stacking and orientations were found depending on the substrate and the molecular structure. However, a complete vibrational characterization of these materials by Raman and IR is not available. The present work is the first report

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on Raman (RS), resonance Raman (RRS), and surface-enhanced resonant Raman scattering (SERRS) of $H_2$-Nc and CuNc. Using the polarization properties of the vibrational transitions, the molecular orientation in vacuum evaporated films was probed by transmission and reflection–absorption FTIR spectroscopy. Far-infrared spectra were also recorded and vibrational assignment for both molecules was attempted. Scanning electron microscopy (SEM) and TEM images were obtained for film structural characterization. For comparison with other mono- and di-Pc materials in potential sensor applications, the adsorption of $NO_2$ on vacuum evaporated films of both materials was followed using visible absorption spectroscopy and SERRS.

## Experimental Section

Metal-free and copper 2,3-naphthalocyanines ($H_2$Nc and CuNc) were purchased from Aldrich Chemical Co. and identified by IR and UV–vis spectroscopy. Thin films (25 nm mass thickness) were sublimed in vacuum ($8 \times 10^{-4}$ Pa) onto KBr substrates and smooth Ag films at ambient temperature using a Balzers evaporating system. Film thickness was monitored using an XTC Inficon quartz crystal oscillator. Smooth metal films of 100 nm Ag were made by evaporating silver in vacuum ($2 \times 10^{-4}$ Pa) at a rate of 0.5 nm/s onto a glass substrate maintained at 200 °C. Thin organic films (4 nm mass thickness) of CuNc or $H_2$Nc were evaporated onto SERS substrates consisting of gold island films.[18] Electronic absorption spectra were recorded on a Response UV–visible spectrophotometer interfaced to an IBM-PC. Samples were prepared in KBr pellets for Raman and mid-infrared experiments and in Nujol mulls for the far-infrared measurements. A Spectra Physics Model 2020 $Kr^+$ ion laser was used to obtain the inelastic scattering measured with a Spex-1403 double spectrometer. A Lexel $Ar^+$ laser was used to excite the nonresonance spectra measured with a THR-3000 spectrograph equipped with a liquid nitrogen cooled Spex CCD detector. Infrared spectra were measured on a BOMEM DA3 FTIR spectrometer equipped with a MCT detector and a DTGS pyroelectric detector operating at 300 K. A beamsplitter consisting of a 6 $\mu$m stretched Mylar pellicle was used for the far-infrared measurements. For data analysis, all files were imported to Spectra Calc software available from Galactic Industries Corp.

Thin organic films on Au island and KBr substrate were placed in a 0.4 $dm^3$ cell and exposed to $NO_2/N_2O_4$ gas (Aldrich Chemical Co., 99.5%). The cell was evacuated first, and then gas was admitted. The films were exposed to the gas for 1 min.

For TEM, SEM, and electron diffraction measurements, thin films of CuNc or $H_2$Nc (40 nm thickness) were evaporated onto glass slides (Corning 7059) held at ambient temperature. TEM and electron diffraction measurements were carried out using a JEOL-CX100 transmission electron microscope. SEM images were obtained with a Nanolab 7 scanning electron microscope. For TEM observations, the films on glass were exposed to hydrofluoric acid vapor, floated off on a water surface, and transferred to copper microscope grids. For SEM measurements, the floating film was stuck on an aluminum stub and then coated with gold. The diffused rings in the electron diffraction pattern showed that the materials in the film were amorphous. The scanning and transmission electron micrographs for CuNc are shown in Figure 2. The CuNc film deposited onto a glass surface at 25 °C consists of small needlelike microcrystals as shown in the TEM micrograph of Figure 2. The morphology is very similar to that of VONc thin film deposited onto a KCl crystal surface at 150 °C.[12]

## Results and Discussion

**Infrared Spectra.** The static molecular geometry of $H_2$Nc shown in Figure 1 indicates a $D_{2h}$ point-group

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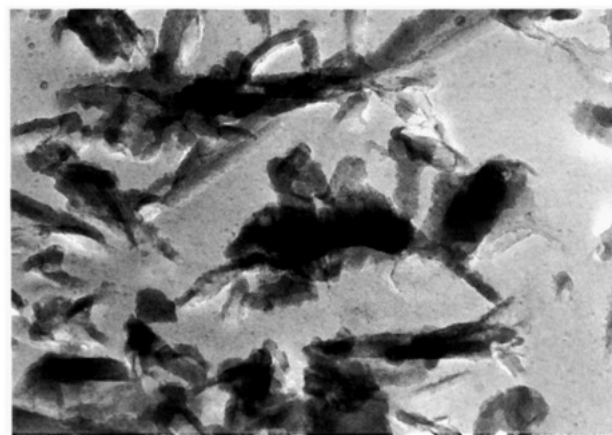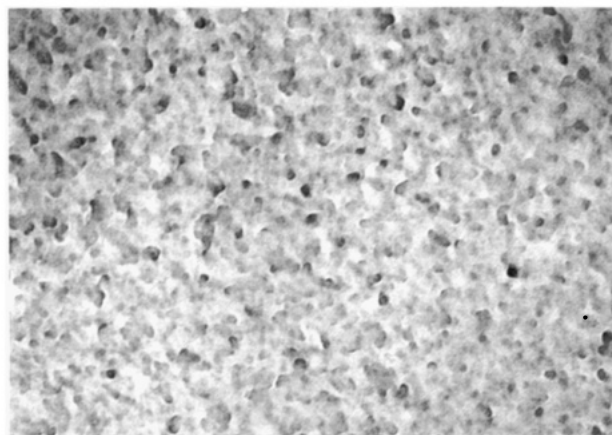


**Figure 2.** Scanning and transmission electron micrographs of CuNc.

symmetry. There are 240 normal modes, and the total irreducible representation contains $\Gamma = 41\ a_g + 40\ b_{1g} + 19\ b_{2g} + 20\ b_{3g} + 19\ a_u + 21\ b_{1u} + 40\ b_{2u} + 40\ b_{3u}$. The molecular model of CuNc belongs to the $D_{4h}$ point-group symmetry, with a total representation $\Gamma = 20\ a_{1g} + 19\ a_{2g} + 20\ b_{1g} + 20\ b_{2g} + 19\ e_g + 9\ a_{1u} + 11\ a_{2u} + 10\ b_{1u} + 10\ b_{2u} + 40\ e_u$.

The observed vibrational frequencies for $H_2$Nc and CuNc are given in Tables 1 and 2. For both molecules, it was observed that several frequencies were active in the IR and Raman spectra, indicating the absence of centrosymmetric symmetry or, alternatively, a large number of accidental degeneracies. It has been speculated that the planar molecules in the solid could be deformed "warped macrocycles",[17] and the present vibrational data seem to support this assumption. The descent symmetry point group could be $C_{2v}$ and $C_{4v}$ for $H_2$Nc and CuNc respectively. For a $C_{2v}$ group there will be 81 $a_1$ totally symmetric vibrations active in the Raman spectrum. The descent in symmetry to $C_{4v}$ would render 31 $a_1$ totally symmetric Raman active vibrations. The assignment given in the tables is restricted to characteristic fundamentals, and is based on previous descriptions of normal modes for naphthalene[19,20] and Pc molecules.[21-23]

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**Table 1.  Vibrational Frequencies (cm⁻¹) for CuNc in KBr Pellet**

| LL = 647.1 nm | LL = 514.5 nm | IR | tentative assignment |
|---|---|---|---|
| 223 (20) | 221 (5) | | Cu−N stretching |
| 296 (8) | | | |
| | 474 (5) | 470 (50) | |
| | | 497 (25) | |
| 511 (6) | 517 (7) | | |
| 531 (27) | 540 (21) | | |
| | 555 (16) | | |
| | | 568 (9) | |
| 615 (46) | 615 (8) | 619 (7) | |
| | 648 (16) | | |
| 681 (79) | 680 (26) | | Nc breathing |
| | | 715 (41) | |
| 735 (24) | 722 (18) | | |
| 756 (20) | 756 (12) | 752 (96) | C−H wag |
| | 811 (4) | | |
| 845 (20) | 842 (8) | | |
| | 857 (5) | 861 (29) | |
| 873 (16) | 873 (5) | | |
| | | 888 (42) | |
| | | 944 (8) | |
| 1015 (10) | 1012 (9) | 1013 (16) | in-plane C−H bend |
| | 1026 (14) | 1035 (21) | in-plane C−H bend |
| | 1051 (10) | | |
| | 1090 (24) | 1094 (100) | in-plane C−H bend |
| | 1109 (26) | | |
| 1123 (49) | 1127 (28) | 1128 (30) | in-plane C−H bend |
| 1149 (29) | 1151 (34) | 1158 (33) | pyrrole breathing |
| 1187 (76) | 1184 (24) | | in-plane C−H bend |
| | | 1200 (16) | |
| 1213 (33) | 1215 (34) | | in-plane C−H bend |
| | | 1262 (15) | in-plane C−H bend |
| | 1288 (11) | | |
| 1316 (11) | | | |
| | | 1340 (70) | pyrrole stretching |
| 1365 (24) | 1360 (59) | | naphthalene stretching |
| | | 1374 (53) | naphthalene stretching |
| 1398 (67) | | | isoindole stretching |
| 1441 (28) | 1432 (64) | 1432 (22) | isoindole stretching |
| 1475 (7) | | 1470 (36) | isoindole stretching |
| | 1504 (13) | 1515 (22) | pyrrole stretching |
| 1526 (100) | 1527 (27) | | aza stretching |
| | 1603 (100) | 1601 (19) | naphthalene stretching |
| 1629 (10) | 1626 (60) | 1632 (19) | naphthalene stretching |

**Table 2.  Observed Vibrational Frequencies (cm⁻¹) for H₂Nc in KBr Pellet**

| LL = 647.1 nm | LL = 514.5 nm | IR | tentative assignment |
|---|---|---|---|
| 171 (100) | | | benzoisoindole def |
| 285 (12) | 288 (7) | | |
| 478 (20) | 480 (8) | 470 (60) | |
| 528 (36) | 530 (16) | | |
| | 559 (22) | | |
| 611 (22) | 614 (9) | 614 (18) | |
| 679 (93) | 680 (30) | | Pc breathing |
| | | 697 (48) | op N−H def |
| 717 (46) | 717 (12) | 720 (11) | |
| 757 (30) | 758 (34) | 756 (86) | C−H wag |
| 819 (13) | 822 (14) | | |
| 835 (33) | 838 (22) | 835 (35) | |
| 894 (8) | | 891 (53) | op C−H bend |
| | 914 (5) | | |
| | | 943 (11) | |
| | 954 (6) | | |
| | 971 (8) | | |
| | | 1006 (100) | in-plane N−H def |
| 1015 (12) | 1020 (5) | 1019 (49) | in-plane C−H bend |
| | | 1027 (81) | in-plane C−H bend |
| | 1050 (5) | | |
| | 1096 (18) | 1092 (63) | in-plane C−H bend |
| 1120 (87) | 1122 (19) | | in-plane C−H bend |
| 1132 (20) | | 1131 (25) | in-plane C−H bend |
| 1149 (52) | | 1144 (16) | pyrrole breathing |
| | 1164 (38) | 1164 (22) | |
| 1180 (86) | 1183 (64) | | in-plane C−H bend |
| | | 1200 (7) | |
| | | 1212 (10) | |
| | | 1263 (17) | in-plane C−H bend |
| 1309 (17) | 1316 (22) | | |
| | | 1327 (51) | |
| 1352 (50) | 1353 (76) | 1351 (63) | pyrrole stretching |
| | 1366 (82) | 1368 (39) | naphthalene stretching |
| 1394 (58) | | 1390 (49) | naphthalene stretching |
| | 1409 (61) | | isoindole stretching |
| 1422 (30) | 1422 (64) | | isoindole stretching |
| 1437 (11) | | 1441 (20) | isoindole stretching |
| | | 1468 (26) | isoindole stretching |
| | | 1496 (31) | isoindole stretching |
| 1512 (40) | 1507 (32) | 1517 (43) | pyrrole stretching |
| 1540 (71) | 1540 (96) | 1530 (61) | aza stretching |
| | 1598 (92) | 1590 (16) | naphthalene stretching |
| | | 1611 (13) | naphthalene stretching |
| 1627 (15) | 1632 (100) | 1627 (15) | naphthalene stretching |

**Table 3.  Far-Infrared Frequencies (cm⁻¹)**

| H₂Nc | CuNc | H₂Nc | CuNc |
|---|---|---|---|
| | | 289 (67) **Pc** | |
| 168 (35) | | 305 (11) | 307 (27) **Pc** |
| 196 (21) | 185 (100) | 319 (17) | |
| 210 (38) | | 337 (100) **Pc** | 341 (27) **Cu−N** |
| 223 (19) | | 380 (19) | |
| 232 (25) **Pc** | 229 (22) **Pc** | 417 (66) **Pc** | 416 (10) **Pc** |
| 263 (35) **Pc** | 260 (16) | 436 (41) **Pc** | |

The most intense band in the IR spectrum of H₂Nc at 1006 cm⁻¹, absent in CuNc, remains unshifted with respect to the H₂Pc derivative where has been assigned to a N−H deformation mode.[21] The N−H and C−H stretching vibrations were observed at 3290 and 3052 cm⁻¹ for H₂Nc; the C−H stretching for CuNc was at 3050 cm⁻¹. The N−H out-of-plane (op) deformation in H₂Pc has been assigned at 716 cm⁻¹. By comparison of the infrared spectra of CuNc with that of the H₂Nc, it can be seen that the 697 cm⁻¹ in H₂Nc was not observed in CuNc. It seems reasonable to assign the 697 band to the op N−H vibration. There are several op C−H bending vibrations in naphthalene in the 700−800 cm⁻¹ region. Considering the benzoisoindole moiety, the strong band at 752 cm⁻¹ in CuNc and the strong and broad band at 756 cm⁻¹ in H₂Nc should be assigned to the C−H wag fundamental. In-plane C−H bending vibrations are localized in the region 1000−1270 cm⁻¹ in the IR spectrum of naphthalene. By analogy, bands at 1019, 1027, and 1092 cm⁻¹ are assigned to the in-plane C−H bending modes of the benzoisoindole units in H₂Nc. Similar bands at 1013, 1035, and 1094 cm⁻¹ were observed for CuNc.

Characteristic C−C and C−N stretching vibrations are detected in the 1300−1600 cm⁻¹ region, and for instance in the spectrum of naphthalene there are six C−C stretching frequencies above 1500 cm⁻¹. Therefore, vibrational frequencies observed at 1627, 1611, and 1590 cm⁻¹ in H₂Nc and 1632 and 1601 cm⁻¹ in CuNc can be assigned to the C−C stretching vibrations of the

naphthalene ring. The 1351 cm⁻¹ band in the IR spectrum of H₂Nc and the 1340 cm⁻¹ band in that of CuNc are characteristic C−C stretching vibrations of the pyrrole moiety in the Pc ring. The C−N stretching vibrations of the pyrrole moiety are also clearly seen at 1517 cm⁻¹ in H₂Nc and at 1515 cm⁻¹ in CuNc. Similar bands are also observed in the Raman spectra with strong relative intensity. Notably, the IR spectrum of the CuNc in KBr pellet twins the reported IR spectrum of ZnNc in the 700−1500 cm⁻¹.[16]

The observed vibrational frequencies in the far-infrared spectra of the samples dispersed in Nujol mulls are listed in Table 3. Vibrational modes in this spectral region are highly coupled, and only normal modes with a large contribution from a metal−nitrogen bond are assigned. The assignment of the M−N stretching and bending vibrations has been attempted for a number of mono- and di-Pc derivatives.[24−26] In particular, for CuPc, bands at 285 and 352 cm⁻¹ were found to have a
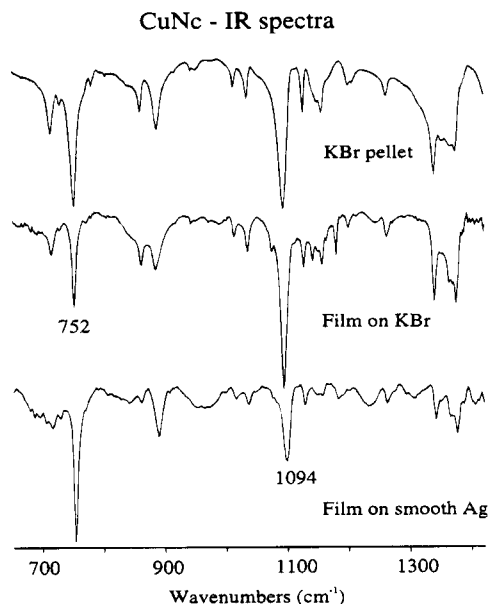
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CuNc - IR spectra



**Figure 3.** FTIR spectra of CuNc. Top: in a KBr pellet. Middle: evaporated film on KBr. Bottom: evaporated film on smooth Ag substrate.

large Cu$-$N stretching contribution, and the ring deformation at 151 cm$^{-1}$ also showed a Cu$-$N dependence. The Cu$-$N stretching mode could be assigned to the 341 cm$^{-1}$ band in the far-IR spectrum. For comparison, we have plotted the far-IR of H$_2$Nc and H$_2$Pc. Consistently, all the bands observed in the H$_2$Pc are seen in the spectrum of H$_2$Nc with a similar frequency. However, the relative intensities are very different and the H$_2$Nc contains a number of other frequencies that should be related to the naphthalene moieties. In Table 3, all bands with H$_2$Pc (and CuPc) counterparts have been marked **Pc**.

**Molecular Orientation in Evaporated Thin Films.** The fact that vibrational transitions are polarized along a particular molecular axis permits the use of RAIRS and transmission FT-IR to probe the molecular orientation in thin solid films. In the RAIRS experiment, surface selection rules[27-29] lead to the manifestation of molecular vibrations with a finite nonzero component of their dynamic dipole perpendicular to the metal surface, whereas in the transmission geometry light at normal incidence will interact with vibrations which generate a change in the dipole moment in the substrate plane. The reference for both the RAIR and the transmission IR analyses is a random distribution of molecules in the sample (KBr pellet), where the relative intensities can be considered to be the result of the spatial average of transition dipole moments interacting with the external electric field. For an ideal flat molecule in a face-on molecular organization, in-plane vibrations would have a maximum relative intensity in the transmission spectrum and a minimum intensity in the RAIR spectrum. The reference, the transmission and the RAIR spectra for CuNc are shown in Figure 3.
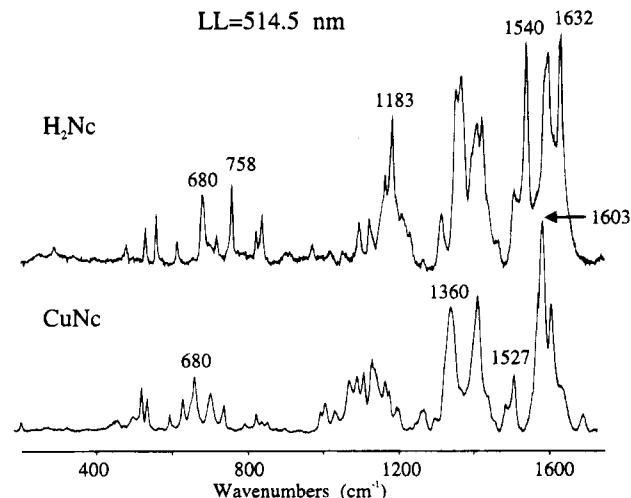
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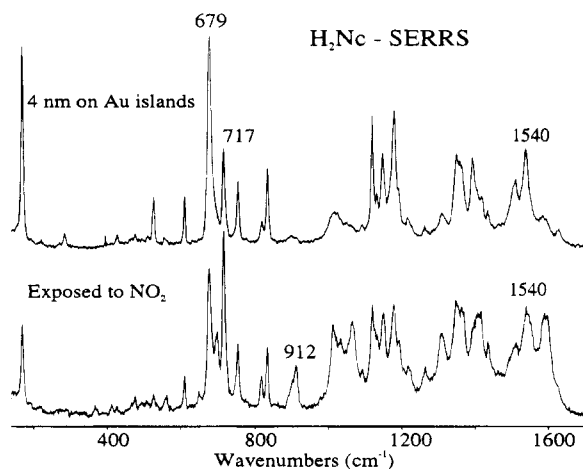(29) Moskovits, M. *J. Chem. Phys.* **1982**, *77*, 4408.



**Figure 4.** Spontaneous Raman scattering (LL = 514.5 nm) of H$_2$Nc and CuNc in KBr pellets.

To simplify the discussion, the strong band of the in-plane C$-$H bending mode at 1094 cm$^{-1}$ (polarized in the molecular plane) and the out-of-plane wag at 752 cm$^{-1}$ (polarized perpendicular to the molecular plane) can be selected. In the transmission spectrum of the evaporated film, the relative intensity of the C$-$H wag at 752 cm$^{-1}$ has decreased if compared with that of the in-plane C$-$H bending mode. The opposite trend is observed in the RAIR spectrum, where the C$-$H wag is clearly the strongest band in the spectrum. Therefore, both transmission and RAIR results suggest a molecular organization with a nearly face-on **or tilted** molecular orientation in the evaporated films on silver and KBr. Yanagi et al.[16,17] have also reported a **tilted** (nearly face-on) organization for H$_2$Nc and ZnNc films as revealed by transmission and reflection$-$absorption IR spectroscopy, in agreement with our own results for evaporated films of CuNc and H$_2$Nc onto KBr and Ag. It should be noticed that the only reported evaporated film with an average face-on orientation (complete disappearance of the in-plane modes in the RAIRS spectrum) is that of the ZnNc evaporated onto a single NaCl crystal.[16]

**Raman Spectra.** The electronic absorption spectra of evaporated films (25 nm thickness) of H$_2$Nc and CuNc on KBr substrates show a broad absorption band at ca. 716 nm with a shoulder at ca. 800 nm, in agreement with previous reports.[2,11] Excitation with the 514.5 nm laser line leads to spontaneous Raman scattering (RS) whereas the spectra obtained with the 647.1 nm laser line are in resonance with the absorption band (RRS). The RS spectra of H$_2$Nc and CuNc dispersed in KBr pellets are given in Figure 4. A comparison with RS spectra of the Pc derivatives (H$_2$Pc and CuPc)[19,20] shows that although the Nc spectra contain most of the frequencies found in the mono-Pc complexes, the relative intensities are clearly different. For instance, the strongest bands in the RS spectra of Nc molecules correspond to the C$-$C stretches of naphthalene at 1632 and 1598 cm$^{-1}$ in H$_2$Nc and 1626 and 1603 cm$^{-1}$ in CuNc. However, the resonance Raman spectra of H$_2$-Nc and CuNc are very similar to those of H$_2$Pc and CuPc: a strong Pc breathing at 679 cm$^{-1}$ in H$_2$Nc and 681 cm$^{-1}$ in CuNc, a group of C$-$H bending modes in the 1100$-$1250 cm$^{-1}$ and the pyrrole ring and aza groups stretches in the 1500 cm$^{-1}$ region. In the RRS spectra, the vibrational modes of the chromophore (Nc macrocycle) are selectively enhanced. RRS spectra are

**Figure 5.** Surface-enhanced resonant Raman spectra of H₂-Nc and H₂Nc-NO₂ on Au island film.



**Figure 6.** Surface-enhanced resonant Raman spectra of CuNc and CuNc-NO₂ on Au island film.

identical with the SERRS spectra of evaporated films (4 nm mass thickness) on Au island films, which are shown in Figures 4 and 5. The strong intensity of the 171 cm$^{-1}$ band in the RRS or SERRS spectra of H₂Nc is a peculiar feature in this molecule. This band could be assigned to the in-phase motion of the benzoisoindole groups, a totally symmetric vibration. The presence of the metal seems to hinder this vibration, and in CuNc the only medium-intensity band in this region is observed at 223 cm$^{-1}$ and is probably a deformation with a large Cu–N stretching contribution.

C–H bending modes at 1240 and 1144 cm$^{-1}$ in the Raman spectrum of naphthalene can be correlated to those observed at 1213, 1187, and 1123 cm$^{-1}$ in CuNc and 1180, 1132, and 1120 cm$^{-1}$ in H₂Nc. Frequencies and tentative assignments are given in Tables 1 and 2.

**Gas–Solid Adsorption.** The interaction of Pc molecules with electron-acceptor gases like NO₂ is known to change the electrical properties of the material, increasing the electrical conductivity due to the formation of a "doped organic semiconductor".[30] The chemisorption reaction Nc–NO₂ is of interest in its own right, and the change in electrical properties could have applications in sensor technology. Recently, we have shown that for a number of Pc derivatives the reversible adsorption of NO₂ on a single LB monolayer can be monitored using SERRS.[31-33] The formation of quality LB films of neat CuNc and H₂Nc was not successful due to low solubility and aggregation of the Nc molecules. Therefore, vacuum-sublimated films of CuNc and H₂-Nc were prepared on KBr substrates (25 nm thickness) and on Au island films (4 nm thickness), and were exposed to NO₂/N₂O₄ gas. The effects of gas adsorption were monitored in the visible absorption, RRS, and SERRS spectra, and it was found that the NO₂ adsorption was not totally reversible. The interaction with the gas broadens the red bands, and the center is shifted from 716 to 744 nm and from 720 to about 766 nm in the electronic spectra of CuNc and H₂Nc, respectively. The SERRS spectra of the 4 nm thick films on Au after being exposed to NO₂ gas are also shown in Figures 5 and 6. Notably, only a partial recovery of the original
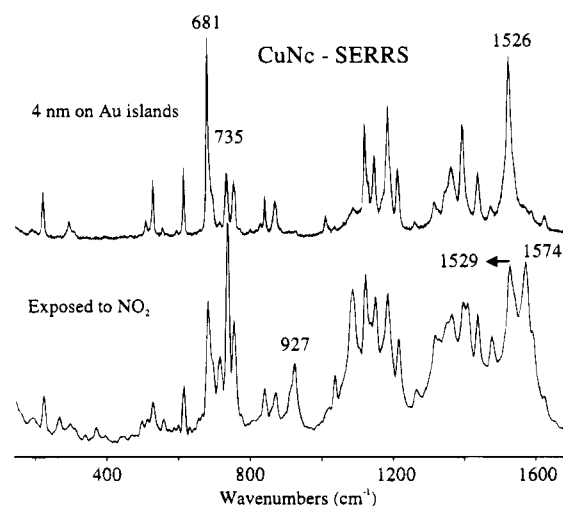
spectra was observed even after expediting desorption by vacuum and heating. The effect of the NO₂–macrocycle interaction is evident in the SERRS spectrum of the chromophore, where the relative intensities of the macrocycle frequencies are diminished (polarization by NO₂). However, as can be seen in Figure 5, naphthalene bands at 717, 1590, and 1598 cm$^{-1}$ are seen with enhanced relative intensity in the spectrum of H₂Nc, and a new band at 912 cm$^{-1}$ was recorded. Similarly, naphthalene bands at 737 and 1574 cm$^{-1}$ for CuNc become prominent in the CuNc–NO₂ spectra, and a new band at 927 cm$^{-1}$ is seen. The bands at 912 and 927 cm$^{-1}$ may be related to the NO₂ itself. In conclusion, the SERRS spectra provide some evidence of NO₂ interaction with the center of the macrocycle which gives rise to stronger bands corresponding to the peripheral naphthalene moieties. The NO₂ chemisorption is not completely reversible and the spectral features of the Nc–NO₂ adduct were observed in the SERRS spectra even after keeping the film under vacuum (3 × 10$^{-4}$ Pa) at 200 °C for 2 h. However, partial desorption of NO₂ takes place since the relative intensity pattern in the 679–717 cm$^{-1}$ in H₂Nc and 681–735 cm$^{-1}$ in CuNc is partially recovered and the intensity of the 912 and 927 cm$^{-1}$ bands decreases.

**Conclusion**

The vibrational characterization of H₂Nc and CuNc and of their vacuum-evaporated films is given based on RRS, SERRS, and middle- and far-infrared spectra. Since RRS and SERRS spectra on Au are identical, characteristic Raman frequencies of Nc molecules given here may be used in detection of picomole quantities of Nc materials. A tilted, close to face-on molecular orientation in the evaporated films on KBr and Ag was inferred from the transmission and RAIR spectra. Film morphology images obtained using scanning and transmission electron microscopy are also given. Spectroscopic evidence was found showing that H₂Nc and CuNc molecules in evaporated films exposed to NO₂ form stable adducts. SERRS and RRS spectra showed that the NO₂ chemisorption is not completely reversible, and complete desorption of NO₂ was not achieved under vacuum or heating.

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