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Vapor Sensing

Three-Dimensional Solvent-Vapor Map Generated by Supramolecular Metal-Complex Entrapment**

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Supramolecular assemblies have become increasingly popular over the past few years,[1] especially in areas such as catalysis,[2,3] gas sequestration,[4] and separation.[3,5] Similarly, interesting approaches for the detection of toxic gases and vapors of volatile organic compounds (VOCs) have been studied to develop an artificial nose that is capable of identifying these species in an unambiguous and simple way.[6] The use of supramolecular and crystalline arrays of metal complexes with electronic transitions that are sensitive to the presence of a variety of volatile molecules,[7] has received considerable attention.[8–10] However, although metal complexes of platinum,[9] gold,[10] palladium,[11] and copper[12a,b] have been widely employed for vapor detection, rhenium has been rarely used.[12c] Herein, we propose to use a zeolite framework for the supramolecular assembly of rhenium complexes with applications to vapor sensing.

Zeolites are aluminosilicates with a repeating microporous structure composed of {AlO_4} and {SiO_4} building blocks.[13] The internal framework is a network of cavities (supercages) that are interconnected by channels (Figure 1 a). This architecture allows zeolites to act as molecular sieves, with applications ranging from catalysis[14] to light-harvesting systems.[15] Because of their porous structure, ion-exchange properties, and molecular and size recognition, many ions and molecules have been immobilized within zeolites.[16] Particularly relevant for this research, the photoluminescent tris(2,2′-bipyridine)ruthenium(II) complex ($[Ru(bpy)_3]^{2+}$) has been encapsulated in NaY and thoroughly studied.[17] As the pore diameter of the NaY framework is smaller than the diameter of $[Ru(bpy)_3]^{2+}$, this molecule is synthesized in situ by a ship-in-the-bottle method.[18] This method involves the loading of NaY with a ruthenium salt, followed by the addition of 2,2′-bipyridine as a ligand. The $[Ru(bpy)_3]^{2+}$ complex is formed inside the supercage, and therefore it becomes entrapped within the zeolite. The material is fundamentally composed of a zeolite framework, with the supercages occupied by individual $[Ru(bpy)_3]^{2+}$ ions, thus forming a true solid solution.

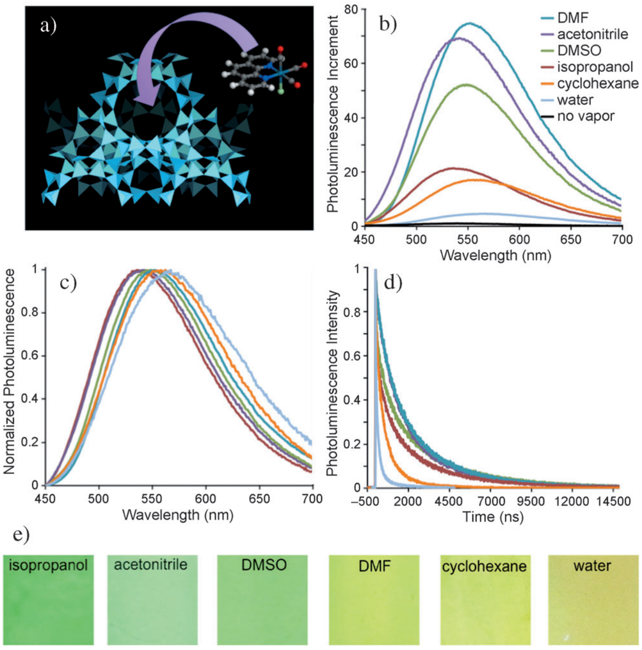

Figure 1. Effect of solvent vapors on the photophysical properties of [Re(phen)(CO)$_3$Cl]@NaY. a) Representation of the NaY zeolite showing one of the supercavities where [Re(phen)(CO)$_3$Cl] can be entrapped. b) Photoluminescence spectra of [Re(phen)(CO)$_3$Cl]@NaY upon treatment with different solvent vapors showing the change in emission intensity (no vapor: material before exposure to vapor, with a photoluminescence adjusted to unity). c) The normalized photoluminescence, which was obtained from the spectra in (b), emphasizes the change in photoluminescence maxima with different vapors. d) Time-resolved photoluminescence decays of [Re(phen)(CO)$_3$Cl]@NaY under different solvent vapors. e) Digital photographs of vapor-treated [Re(phen)(CO)$_3$Cl]@NaY material under UV light. DMF = *N*,*N*-dimethylformamide, DMSO = dimethyl sulfoxide.

Inspired by the aforementioned reports, we used the ship-in-the-bottle method to synthesize [Re(phen)(CO)$_3$Cl] (phen = 1,10-phenanthroline) in the cavities of the NaY zeolite. The ligands and the metal react in the NaY supercages to form the [Re(phen)(CO)$_3$Cl] complex. The supercages of the NaY zeolite have a diameter of approximately 13 Å (large enough to accommodate the complex with a diameter of ca. 9 Å)[19] and pore entrances of approximately 7.4 Å. Therefore, the rhenium complex can fit into the supercage, but once it has been entrapped inside, it is too large to diffuse out of the cage through the pore entrance. To the best of our knowledge,

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this is the first report of an encapsulation of [Re(phen)(CO)$_3$Cl] within the NaY zeolite.

Herein, we report the use of the [Re(phen)(CO)$_3$Cl] complex encapsulated within a faujasite NaY zeolitic framework ([Re(phen)(CO)$_3$Cl]@NaY) as a photoluminescent sensor for solvent vapors (Figure 1 a). Upon exposure to solvent vapors, the [Re(phen)(CO)$_3$Cl]@NaY material features vapoluminescence (a change in the photoluminescence intensity) and luminescence vapochromism (a change in the photoluminescence maximum). Interestingly, we also observed changes in the photoluminescence lifetime of the material upon vapor treatment, and we term this behavior vapotemporism. To the best of our knowledge, changes in the photoluminescence lifetime have not been systematically used in the context of vapor detection thus far. By determining just three photophysical parameters of this material upon exposure to solvent vapors (photoluminescence intensity, emission wavelength, and lifetime), unambiguous identification of the vapors may be achieved by correlation with a simple 3D vapor map. The results explained below illustrate a novel way of identifying and classifying vapors of volatile species.

The material obtained by the encapsulation of [Re(phen)(CO)$_3$Cl] within the NaY zeolite framework was analyzed by IR spectroscopy (Supporting Information, Figure S1). The NaY zeolite showed two major bands at 3500 and 1640 cm^{-1}, which are assigned to the bending vibrations of lattice water molecules and surface silanol groups, respectively (Supporting Information, Figure S1 a).[20] For [Re(phen)(CO)$_3$Cl], two closely spaced bands at approximately 1890 and 1920 cm^{-1} that are due to two equatorial CO stretching modes and a sharper band at about 2013 cm^{-1} that is due to an axial CO stretching vibration were observed (Figure S1 b).[21] The IR spectrum of [Re(phen)(CO)$_3$Cl]@NaY may be considered as a superposition of the spectra of [Re(phen)(CO)$_3$Cl] and NaY (Supporting Information, Figure S1 c). This provides evidence for the formation of [Re(phen)(CO)$_3$Cl] and for the fact that neither the NaY framework nor the complex have undergone significant changes in their structure that are caused by the encapsulation procedure.

The absorption and photoluminescence spectra of [Re(phen)(CO)$_3$Cl] encapsulated within the NaY framework were also investigated. The diffuse reflectance of the material and a UV/Vis spectrum in acetonitrile (MeCN) were obtained for [Re(phen)(CO)$_3$Cl]@NaY and [Re(phen)(CO)$_3$Cl], respectively (Supporting Information, Figure S2). We observed a blue-shift of approximately 5 nm of the metal–ligand charge transfer (MLCT) band of [Re(phen)(CO)$_3$Cl] @NaY with respect to the corresponding band of [Re(phen)(CO)$_3$Cl] in acetonitrile solution. This blue-shift is consistent with studies of [Re(phen)(CO)$_3$Cl] at 77 K in ether–isopentane–alcohol glass (EPA).[22] The photoluminescence spectrum of [Re(phen)(CO)$_3$Cl]@NaY show a large blue-shift compared with [Re(phen)(CO)$_3$Cl] in acetonitrile (Supporting Information, Figure S3). The corrected emission maxima of a [Re(phen)(CO)$_3$Cl]@NaY film and [Re(phen)(CO)$_3$Cl] in acetonitrile are 542 nm and 625 nm, respectively. The large blue-shift upon encapsulation in NaY can be explained by photoluminescence rigidochromism, as previously described by Wrighton and Morse for this kind of complexes.[22,23] Blue-shifts of emission maxima were also observed when [Ru(bpy)$_3$$^{2+}$] was encapsulated within zeolite supercages[24] or zirconium–phosphate layers.[25]

Photoluminescence lifetimes were studied in air for the [Re(phen)(CO)$_3$Cl@NaY] solid material and in nitrogen-purged solutions for [Re(phen)(CO)$_3$Cl]. The luminescence decay of [Re(phen)(CO)$_3$Cl]@NaY could best be fitted to a biexponential decay model with values of 137 and 737 ns (average lifetime $\bar{\tau} = 541$ ns; for calculations, see the Supporting Information); the luminescence lifetime of [Re(phen)(CO)$_3$Cl]@NaY is longer than the lifetime of [Re(phen)(CO)$_3$Cl] dissolved in acetonitrile and dichloromethane solutions, which follows a monoexponential decay model (180 ns and 306 ns, respectively). Wrighton and Morse have demonstrated that the emissive excited state of the [Re(phen)(CO)$_3$Cl] complex has a strong triplet character, which certainly explains the relatively long lifetime of this complex.[22] Furthermore, they showed that the emission maximum depends on the polarity and rigidity of the medium. As the environment become more rigid, the emission become more intense, blue-shifted, and longer-lived, which is a manifestation of the rigidochromic effect.[22] This is consistent with the observation that [Re(phen)(CO)$_3$Cl] encapsulated within NaY has a longer emission lifetime and a shorter emission wavelength than the complex dissolved in dichloromethane and acetonitrile solutions.

To determine whether [Re(phen)(CO)$_3$Cl] is merely adsorbed onto the surface or truly encapsulated within the NaY framework, [Re(phen)(CO)$_3$Cl] was dissolved in dichloromethane and put in contact with NaY. Given that the effective diameter of [Re(phen)(CO)$_3$Cl] (9 Å) is larger than the pore size of NaY (7.4 Å), using this method, the immobilization of [Re(phen)(CO)$_3$Cl] in NaY occurs by impregnation on the outer surface. The emission maximum of the impregnated material is red-shifted by 10 nm relative to the maximum observed for [Re(phen)(CO)$_3$Cl]@NaY (552 and 542 nm, respectively). Furthermore, the photoluminescence lifetime is much shorter (biexponential decay with lifetimes of 4 and 58 ns, $\bar{\tau} = 51$ ns) for the impregnated material than for [Re(phen)(CO)$_3$Cl]@NaY (137 and 737 ns, $\bar{\tau} = 541$ ns). These results suggest that our experimental procedure produces a material with [Re(phen)(CO)$_3$Cl] encapsulated within the interior cavities of NaY, as [Re(phen)(CO)$_3$Cl] impregnated on the surface is not detected.

The photoluminescence of [Re(phen)(CO)$_3$Cl]@NaY films is sensitive to the presence of solvent vapors (for details on film preparation, see the Supporting Information, Scheme S1). Specifically, a general enhancement of the photoluminescence intensity (vapoluminescence) and lifetime (vapotemporism), as well as shifts in the photoluminescence maximum (luminescence vapochromism) were seen when [Re(phen)(CO)$_3$Cl]@NaY films were exposed to different solvent vapors. The changes in intensity of the emission of [Re(phen)(CO)$_3$Cl]@NaY exposed to a variety of vapors is shown in Figure 1 b. This change in intensity can amount from a 5-fold (water) to a 75-fold increase (DMF). The normalized photoluminescence spectra of [Re(phen)$(CO)_3$Cl]@NaY upon exposure to vapors are shown in Figure 1 c, which highlights the shifts in the photoluminescence maximum. These changes in the photoluminescence maximum directly affect the color of the emitted light (Figure 1 e). Similarly, the photoluminescence lifetime of [Re(phen)$(CO)_3$Cl]@NaY is influenced by exposure to vapors (Figure 1 d). For example, significant increments in lifetime were observed when the films were exposed to polar aprotic solvent vapors, such as those of MeCN, DMF, and DMSO; the values obtained are comparable to the lifetime of [Re(phen)$(CO)_3$Cl] in a polyester resin (3670 ns).[22] Shorter lifetimes were obtained for non-polar and protic solvents, with the lowest value measured for water vapor.

Interestingly, we observed that each solvent vapor produces a unique combination of photophysical parameters (emission maximum, intensity, and lifetime), which can therefore be used as a fingerprint for the identification of a specific solvent. Figure 2 a shows a 3D plot of the three photophysical parameters studied (for a complete collection of the photophysical parameters, including error bars, see the Supporting Information, Table 1). Each of these points represents the average of at least three independent experiments; the results were remarkably reproducible. More interestingly, it appears that vapors with certain features (e.g., polarity) tend to present comparable properties, and therefore cluster in specific regions in the 3D space. This has allowed us to identify regions in the 3D map where solvents group together depending on their characteristics. Four different regions of the solvent map are shown in Figure 2 b. Polar aprotic solvents, for example, lead to blue-shifted emissions, large increases in emission intensity, and longer lifetimes, which puts them in the upper left part of the map. On the other hand, the vapors of protic solvents, such as water and ammonia, lead to shorter lifetimes and red-shifts, which puts them in the lower right part of the map. The exposure to alcohols leads to lifetimes and emission maxima that slightly overlap with those obtained for the vapors of aprotic solvents; their increase in photoluminescence, however, is rather similar to that of non-polar vapors, which puts them in a different region in the 3D map. With this 3D map in hand, the classification of an unknown vapor into one of these categories may be achieved by considering solely the photophysical parameters derived from its interaction with [Re(phen)$(CO)_3$Cl]@NaY.

The question remains as to why there are such changes in emission intensity, emission maximum, and lifetime on treating [Re(phen)$(CO)_3$Cl]@NaY with solvent vapors. Changes in the photoluminescence maximum could be explained by specific interactions of the solvent vapors with [Re(phen)$(CO)_3$Cl] causing either stabilization or destabilization of the energy level for the emissive excited state, which would lead to increases (blue-shift) or decreases (red-shift) in the energy gap.[26,27] The changes in the photoluminescence maximum of [Re(phen)$(CO)_3$Cl]@NaY with vapors are different from what has been observed for [Re(phen)$(CO)_3$Cl] dissolved in different solvents,[28] which emphasizes the influence of the NaY framework on the photophysical properties of [Re(phen)$(CO)_3$Cl]. In line with these results, it is reasonable to assume that in dry material, the [Re(phen)$(CO)_3$Cl] complexes strongly associate with the NaY framework, which results in quenching of the photoluminescence intensity and lifetime. The diffusion of solvent vapors into the cavities of the NaY framework disturbs this association, because the solvent vapors interact with both the framework and the metal complex. This will likely diminish non-radiative deactivation processes, thus producing a concomitant increase in photoluminescence intensity and lifetime. Furthermore, an increase in photoluminescence intensity and lifetime while the emission maximum undergoes a blue-shift is consistent with the energy-gap law.[27] Moreover, when [Re(phen)$(CO)_3$Cl]@NaY is exposed to solvent

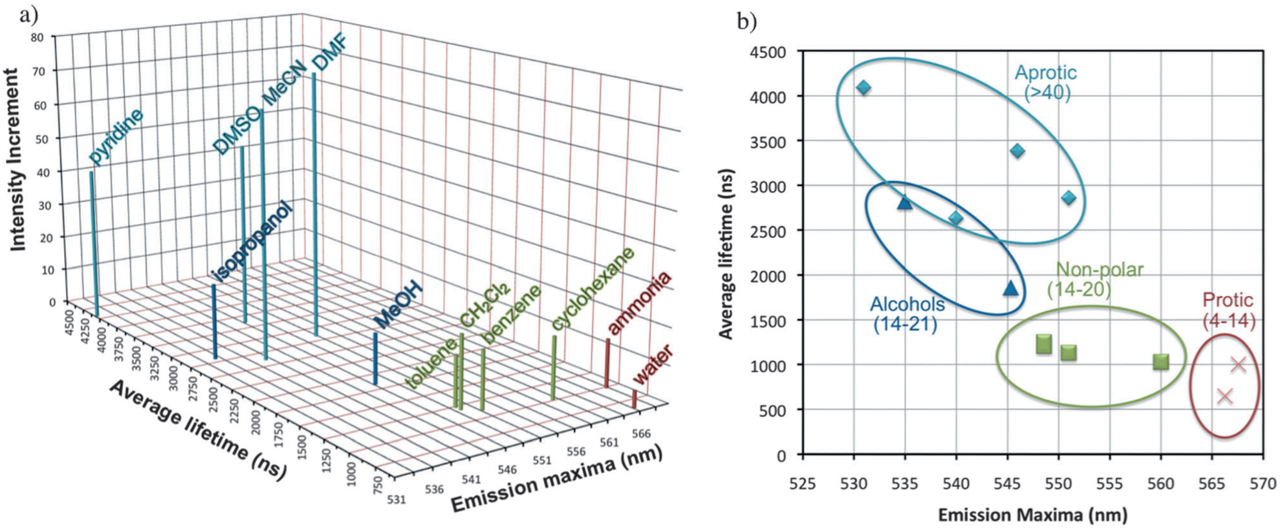

Figure 2. a) Three-dimensional representation of photoluminescence intensities, average lifetimes, and photoluminescence maxima for [Re(phen)$(CO)_3$Cl]@NaY upon exposure to different solvent vapors. b) Flattened 3D map that shows the four distinct regions identified in this study: aprotic, alcoholic, non-polar, and protic solvents. The numbers in parentheses indicate the range of photoluminescence intensities for each region.

vapors, these gases will likely block the zeolite pores and cavities, which inhibits the diffusion of oxygen. As triplet oxygen is an efficient quencher of the excited state of rhenium–diimine–carbonyl complexes,[29] excluding molecular oxygen from the zeolite results in increasing photoluminescence intensity and emission lifetime.

In summary, we have designed a novel platform for detecting solvent vapors based on the entrapment of [Re(phen)(CO)$_3$Cl] within a faujasite–zeolite framework. This material presents vapoluminescence, luminescence vapochronism, and vapotemporism. Our results show that by measuring three simple photophysical parameters (emission intensity, emission maximum, and lifetime) the unambiguous identification of a solvent vapor is achieved. This data was used to build a 3D map, which facilitates the categorization of solvents based on photophysical characteristics. Therefore, the collection of these photophysical parameters for [Re(phen)(CO)$_3$Cl]@NaY exposed to a given vapor will allow: 1) the identification of a given solvent vapor if the spectroscopic parameters are in the database; or 2) the identification of the solvent category (protic, polar aprotic, alcohols, or non-polar) if the vapor has not been previously characterized so that the spectroscopic parameters obtained from [Re(phen)(CO)$_3$Cl]@NaY exposed to this solvent vapor are not in the database. Our approach has desirable properties, such as single-probe detection, easy synthesis, and a simple method that does not require complex statistical or computational analyses to identify the solvent vapor.

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