



SUBDIRECCIÓN GENERAL DE COORDINACIÓN Y
SEGUIMIENTO UNIVERSITARIO
TESIS DOCTORALES - TESEO

Universidad de Castilla-La Mancha

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UNIVERSIDAD DE PROCEDENCIA: Universidad de Castilla-La Mancha

DEPARTAMENTO: Química física

PROGRAMA DE DOCTORADO: Programa de Doctorado en Nanociencia y Nanotecnología por la Universidad de Alicante; la Universidad de Castilla-La Mancha; la Universidad de La Laguna; la Universidad Jaume I de Castellón y la Universitat de València (Estudi General)

CENTRO DE REALIZACIÓN: Facultad de Ciencias Ambientales y Bioquímica de Toledo

TESIS

NOTA:

TÍTULO DE LA TESIS: LASER-BASED SPECTROSCOPY AND FLUORESCENCE MICROSCOPY OF HYDROGEN-BONDED ORGANIC FRAMEWORKS AND THEIR FUNDAMENTAL UNITS: RELEVANCE TO PHOTONIC APPLICATIONS

Sí existe consentimiento para publicar el contenido del fichero de la tesis en Teseo.

RESUMEN: The work of this doctoral thesis is focused on the spectroscopic and dynamic study of a novel class of materials, Hydrogen-Bonded Organic Frameworks (HOFs) and their fundamental units.

HOFs are networks constructed entirely by organic molecules joined by hydrogen bonds. Moreover, for a material to be considered as a HOF it has to be also crystalline, porous and stable. The latter means that the material has to retain the porous structure for a long time under ambient conditions, and after the activation of the HOF, a process that removes the solvent molecules that interpenetrate the network during the synthesis. Since the main driving force for the formation of the HOFs is the hydrogen bonding strength, there is a great variety of organic linkers that can be used as fundamental units. Due to the novelty of these materials (the first synthesized HOF was reported in 2011) the research efforts are predominantly oriented towards the synthesis of new ones, with less attention being paid to study their properties and applications in catalysis, photonics or drug delivery, among others. Hence, there is a large gap in the current understanding about the structure-dynamics relationship in HOF materials. One particular property that has been largely overlooked is their photodynamical behavior. Thus, studying and understanding their luminescence properties can be advantageous for their use in different applications in optoelectronic, photocatalytic or sensor devices.

The studied HOFs in this doctoral thesis have been grouped in two families depending on the fundamental units: (1) HOFs based on hexaazatriphenylenes and (2) HOFs based on dehydrobenzoannulenes derivatives. The photophysical properties of these materials have been studied by a variety of spectroscopic techniques that include ensemble average steady-state and time-resolved emission and absorption covering time scales from femtosecond to millisecond, and single crystal fluorescence lifetime imaging microscopy with picosecond resolution. The studies of the HOFs are complemented by the characterization of the photophysical properties of their corresponding fundamental units.

The fundamental units of CPHAT-1a and CBPHAT-1a (family 1) differ by the presence of one or two, respectively, phenyl groups in the chemical bridge between the core and carboxylic acid. This causes that the pore size of the corresponding HOFs to be different (CPHAT-1a 6.4 Å and CBPHAT-1a 14.5 Å). First, the fundamental units and their methyl derivatives were studied in solution (N,N-dimethylformamide). They present different conformers at the ground state, while their dynamics are governed by an ultrafast intramolecular charge transfer reaction (<15 ps) and proton transfer process, giving rise to the corresponding anions. These results agree with theoretical calculations. The studies of the corresponding HOFs of the two latter fundamental units in solid state show that their photodynamical behavior is governed by the same processes. For CBPHAT-1a a rise of 60 ps was obtained assigned to the time of both processes (charge and proton transfer reactions). The solid state studies for another HOF CPHATN-1a, whose core of the fundamental unit is hexaazatrinaphthalene instead of hexaazatriphenylene, shows a rise shorter (1.1 ps) attributed to both processes. The fluorescence lifetime of the HOFs in this family have values that range from hundreds of picoseconds (200 ps) to few nanoseconds (2.5 ns) assigned to the emission

decays of charge transfer species and also anionic ones. Single crystal fluorescence microscopy studies of these HOFs reveal the preferential orientation of the fundamental units to form the crystals, while showing also the importance of defects and crystal cracking to their photobehaviour. Furthermore, quenching of the emission is observed for CPHAT-1a in presence of iodine, while for CPHATN-1a the same effect is observed in presence of acid vapor. For CBPHAT-1a, the emission quenching is concomitant with the presence of a new red-shifted band in the emission spectrum. These results raise the possibility of using the HOFs from family 1 as fluorescent sensor for the detection of iodine and acids.

The core of the fundamental units of T12-apo and Ex-apo (HOF family 2) are based on dehydrobenzoannulene for the former, while for the latter it is expanded by additional triple bond and a phenyl group. The fundamental units were studied in N,N-dimethylformamide. In the ground state, in addition to being present as monomers, the carboxylic acids interact with the solvent molecules forming different complexes or even giving rise to anions. At the excited state, the species undergo ultrafast charge transfer reaction (<200 fs). The fluorescence lifetimes of the fundamental units of T12-apo (>20 ns) are significantly longer than the ones for Ex-apo (<5 ns). All these results agree with the theoretical calculations. Experiments in solid state of Ex-apo show a photobehaviour similar to its fundamental unit with fluorescence lifetimes that range from hundreds picosecond (100 ps) to few nanoseconds (4.2 ns) corresponding the decay of the charge transfer species and anions following proton transfer reactions, being these two processes ultrafast (<15 ps). The fluorescence microscopy experiments on single crystals exhibit a photobehaviour independent on the interrogated site, while the emission anisotropy shows preferential orientation of the emitters in the crystals. T12-apo crystals of different sizes were studied. The fluorescence of the largest crystals is attributed to species having π - π interactions (20 ns). Additionally, two types of smaller crystals were found each characterized by different photobehaviour. The one of the first type is similar to the one of the large crystals, while the photobehaviour of the second type is governed by species having hydrogen bond interactions and species with anionic character. Moreover, the fluorescence confocal microscopy reveals a strong anisotropic behavior of T12-apo crystals indicating that the fundamental units have preferential orientation in the formed crystal. The observed emission behavior of T12-apo suggests that this HOF could be a candidate for use in white light emitting diodes, when combined with blue-LED.

During three months stay at Hokkaido University under the supervision of Professor Ichiro Hisaki a new HOF (T12F-apo) was synthesized. This new one is based on the introduction of fluorine atoms in the fundamental unit. Although further studies are required to fully characterize the behavior of this HOF, based on previous reports it appears that the introduction of the fluorine atoms in the fundamental unit of the HOF results in a significant increase in the emission quantum yield of the material, making it a potential material for the fabrication of optoelectronic devices. The researches carried out in this doctoral thesis about the photobehaviour of several HOFs and their fundamental units have given rise to six scientific articles. Three of them correspond to HOFs based on hexaazatriphenylene and the other three come from the dehydrobenzoannulene family.

Finally, we have been one of the first groups to report studies on the spectroscopic properties of HOFs, and we believe that these results have helped to understand how important the luminescence properties of these materials are. Furthermore, the use of several spectroscopic techniques (both steady-state and time resolved) have given the ability of deciphering the photodynamic of these HOFs, which we hope will be the basis for further studies on these materials, as well as the potential use of its luminescence in several fields as optoelectronics, biology or technology. These facts could be a great discoveries for the scientific community.



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FIRMA DEL SECRETARIO DEL TRIBUNAL:

FECHA DE LECTURA:

De acuerdo con lo preceptuado en el artículo 17 del Reglamento de los Estudios de Doctorado de la Universidad de Castilla-La Mancha, la secretaria académica de la Escuela Internacional de Doctorado de la Universidad de Castilla-La Mancha, una vez realizado el escrutinio de los votos emitidos por el tribunal que juzgó la tesis doctoral de D. Eduardo Gómez García, defendida el 03/07/2020, ha resuelto **conceder** la mención “*Cum Laude*” a la tesis doctoral titulada “LASER-BASED SPECTROSCOPY AND FLUORESCENCE MICROSCOPY OF HYDROGEN-BONDED ORGANIC FRAMEWORKS AND THEIR FUNDAMENTAL UNITS: RELEVANCE TO PHOTONIC APPLICATIONS”.

Lo que le comunico a Ud. para su conocimiento y efectos oportunos.

Fdo.: Carmen Díaz Delgado
Secretaria de la EID de la UCLM

D. Eduardo Gómez García

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