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Manipulating the Self-assembly of Phenyleneethynylenes under Vibrational Strong Coupling

Kulangara Sandeep,[‡] Kripa Joseph,[‡] Jérôme Gautier,[‡] Kalaivanan Nagarajan,[‡]

Meleppatt Sujith,[†] K. George Thomas,^{*,†} Thomas W. Ebbesen^{*,‡}

[‡] University of Strasbourg, CNRS, ISIS & icFRC, 8 allée Gaspard Monge, 67000
Strasbourg, France

[†] School of Chemistry, Indian Institute of Science Education and Research
Thiruvananthapuram (IISER-TVM), Vithura 695 551, India

Corresponding authors: (KGT) kgt@iisertvm.ac.in; (TWE) ebbesen@unistra.fr

Abstract: The chemical and physical properties of molecules and materials are known to be modified significantly under vibrational strong coupling (VSC). In order to gain insight into the effects of VSC on π - π interactions involved in molecular self-assembly, themselves sensitive to vacuum electromagnetic field fluctuations, the aggregation of two structural isomers (linear and V-shaped) of phenyleneethynylene under cooperative coupling was investigated. By coupling the aromatic C=C stretching band, the assembly of one of the molecules results in the formation of spheres as opposed to flakes under normal conditions. As a consequence, the electronic absorption and emission spectra of the self-assembled structures are also modified significantly. The VSC induced changes depend not only on the type of vibration that is coupled but also on the symmetry of the phenyleneethynylene isomer. These results confirm that VSC can be used to drive molecular assemblies to new structural minima and thereby provide a new tool for supramolecular chemistry.

TOC

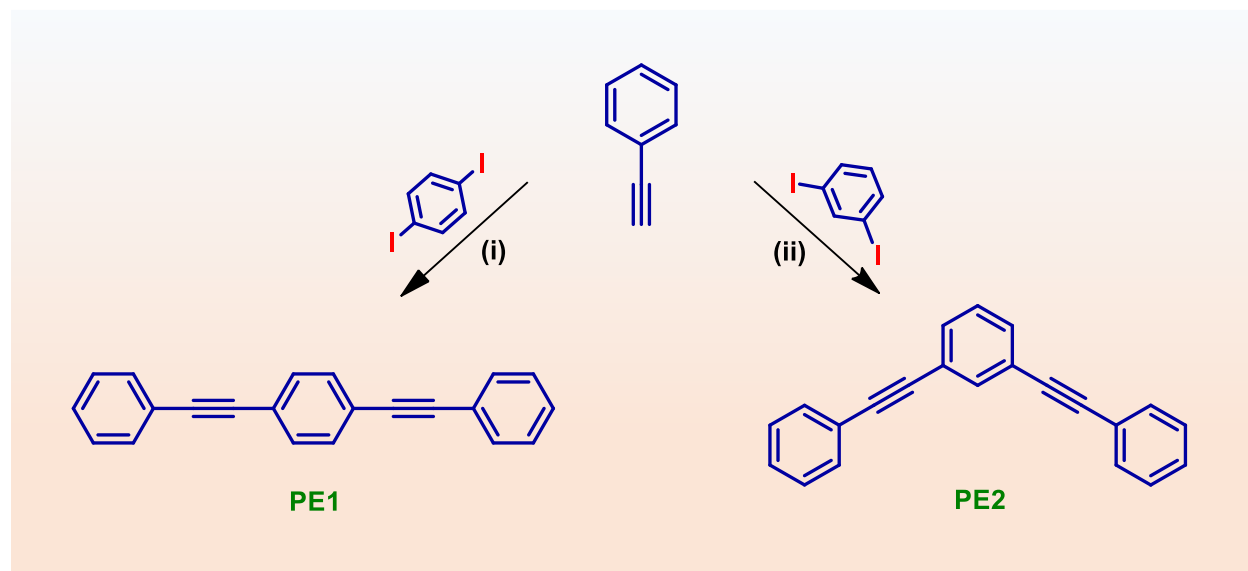


Modulation of the self-assembly of organic molecules to form particular supramolecular structures has enormous importance in chemistry and biology.¹⁻³ Typically, the equilibrium resulting from weak non-covalent interactions leads to the formation of a single thermodynamically favored, supramolecular self-assembly at the nano/micrometer scale.⁴⁻⁶ Factors such as the polarity of the solvent, temperature, light, sound, mechanical force, the concentration of monomer, and electric field are known to perturb such weak noncovalent interactions and thereby the equilibria and the structure of the self-assembled product.⁵⁻¹³ Very recently, it was reported that light-matter strong coupling can also induce changes in intermolecular interactions affecting the self-assembly of a polymer and the polymorphism of a metal-organic framework.^{14, 15}

Light-matter strong coupling has attracted much attention over the past decade as a means to modify a variety of material properties such as chemical reactivity, transport, ferromagnetism, superconductivity, and non-linear optical response.¹⁶⁻⁴¹ In particular, vibrational strong coupling (VSC) has been found to have a very large impact on the chemical and physical properties of molecules.^{17, 18} VSC alters the potential energy surfaces which in turn modify the chemical reaction kinetics and yields, and symmetry has been found to play a fundamental role.^{42, 43} Modification of the potential energy surfaces, as a result of VSC, can also lead to changes in the intermolecular interactions.^{14, 15, 44} In our earlier work, VSC was shown to transform a conjugated polymer gel into flakes.¹⁵ However, the modification of intermolecular interactions, followed by the self-assembly of simple organic molecules under VSC, has not yet been reported. To investigate such possibility, we have studied two structural isomers of phenyleneethynylene (PE) molecules: linear and V-shaped isomers having different polarity. PE type molecules are known to aggregate

through π - π stacking and CH- π interactions.⁴⁵ Interestingly, VSC has a profound effect on the self-assembly of V-shaped isomer but not on the other, as presented below.

The PE molecules (PE1 and PE2) were synthesized by palladium-catalyzed Heck-Cassar-Sonogashira-Hagihara cross-coupling reactions (Scheme 1).^{45, 46} In this synthesis, diiodobenzene is allowed to react with two equivalents of phenylacetylene in the presence of Pd(PPh₃)₂Cl₂, CuI, and triethylamine at room temperature under an inert atmosphere.⁴⁶ Details of the synthesis and characterization (¹H, ¹³C NMR, m/z, and elemental analysis) of the PE are given in the Supporting Information (SI).



Scheme 1: Synthesis of PE molecules: (i) Pd(PPh₃)₂Cl₂, CuI, triethylamine, and tetrahydrofuran. The linear isomer is labeled as PE1 and the V-shaped one as PE2.

VSC experiments were carried out using a microfluidic Fabry-Perot (FP) cavity. The cavity was assembled using two parallel Au mirrors separated with an 8 μ m Mylar spacer.¹⁸ The mirrors were prepared by sputtering 10 nm Au onto the surface of CaF₂ windows.¹⁸ To prevent the direct

interactions between the PE molecules and the Au mirrors, 100 nm of polyvinyl alcohol (PVA) was deposited on the Au surface by spin-coating to act as an insulating layer. Details of the fabrication of FP cavity are given in the SI (see also url: <https://seafire.unistra.fr/d/7bb78e5a4607424f94b5/>). FP cavities will produce many resonant modes separated by fixed energy intervals (the free spectral range or FSR).¹⁸ To achieve VSC, a cavity mode is tuned to the molecular vibration of choice by simply compressing the Mylar spacer between the Au mirrors by adjusting the screws holding the setup together. In a typical experiment, a large number N of molecules are coupled to a resonant optical cavity mode as illustrated in Figure 1. This results in the formation of two bright vibro-polaritonic states, $P+$ and $P-$ and $N-1$ dark states (DS).^{18, 32} The $P+$ and $P-$ states are separated by the Rabi splitting energy ($\hbar\Omega_{vR}$).³² The VSC occurs even in the dark because the coupling involves the zero-point energy of both the optical mode and the vibrational transition.

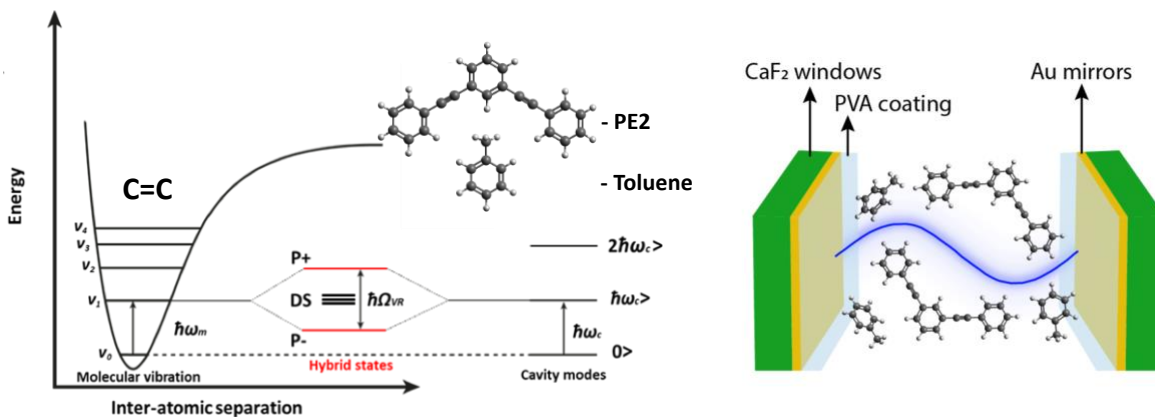


Figure 1: Schematic representation of the generation of polaritonic states, $P+$, $P-$, DS (left panel) as a result of cooperative VSC of toluene and PE molecules in an FP (CaF₂/Au/PVA) cavity (right panel).

The vibrational spectrum of toluene in a cell (i.e., non-cavity made by assembling of two CaF₂ windows coated with PVA separated by a 8 μM Mylar spacer without the Au mirror coating) was recorded and compared with the infrared (IR) spectrum of the PE molecules (Figure 2A,B). The C=C stretching frequency of the toluene and the PE molecules are very close at ca.1603 cm⁻¹, which enables cooperative coupling of toluene and PE. In other words, toluene is strongly coupled and by intermolecular interactions in the solvation shell, it drives the VSC of the resonant PE molecules.^{21, 25} The concentration of the PE molecules was 1 mM in toluene and thus, the absorbance of neat toluene (ca. 9 M) completely dominates at 1603 cm⁻¹. The cavity modes have an FSR 336 cm⁻¹ as shown by the red curve in Figure 2C. The strong coupling was achieved with the 5th cavity mode of the FP cavity at this wavenumber (Figure 2D). The Rabi splitting was found to be 24 cm⁻¹ which is larger than the full width at half maximum (FWHM) of the cavity modes (20 cm⁻¹) and the vibrational transitions (7 and 9 cm⁻¹, toluene and PE respectively), thereby meeting the necessary conditions for VSC. As a control experiment, we made a perfectly off-resonance cavity, where none of the vibrational transitions of toluene and PE are in resonance with the optical modes of the cavity (Figure 2C).

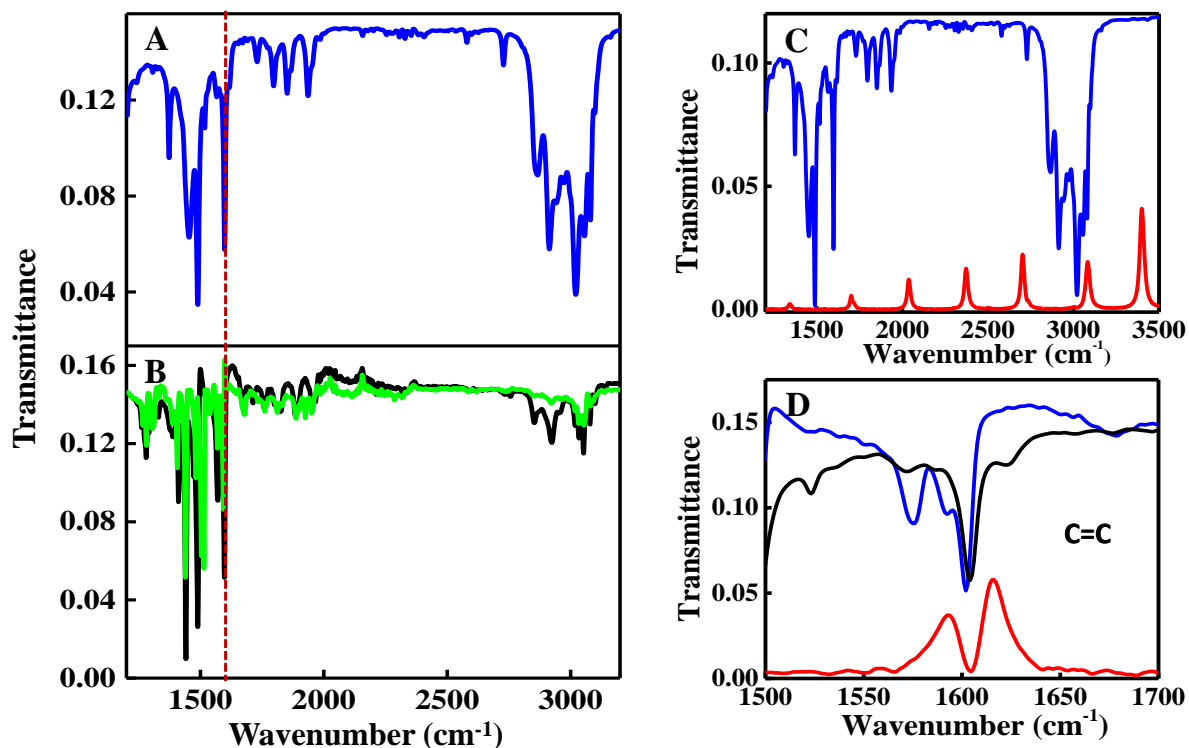


Figure 2: (A,B) Fourier transform infrared (FTIR) spectrum of toluene (A, blue trace) taken in a cell is compared with the attenuated total reflectance IR spectra of PE1 (B, green trace) and PE2 (B, black trace). All the molecules show a vibrational transition around 1603 cm^{-1} , and which facilitates the cooperative strong coupling. (C) FTIR spectrum of the off-resonance cavity, where none of the optical modes (red traces) of the cavity are in resonance with the vibrational transitions of PE and toluene (blue trace). (D) On-resonance cavity where the IR peak at 1603 cm^{-1} of the PE and toluene are coupled with the 5th mode of the FP cavity.

The self-assembly of the PE molecules in toluene in the presence and absence of VSC was then investigated by spectroscopic techniques, and the results are presented in Figure 3 for the PE2 molecule. The experiments were carried out at a fixed temperature ($23\text{ }^{\circ}\text{C}$) with 1 mM PE2, and the absorption was monitored in the presence (Figure 3A) and the absence (Figure 3C) of VSC as

a function of time. As a result of the aggregation, in both cases, we observed a decrease in the absorbance with time. Interestingly, a small but significant difference in the absorption spectrum of the self-assembled structures is found under VSC. It is well known in the literature that the different types of aggregate packing result in a change in electronic absorption and emission properties in such conjugated molecules.^{45,47} Thus, we also checked the fluorescence of the different samples under on-resonance and off-resonance conditions and compared it with the emission spectrum of the monomer (Figure 3B,D). As can be seen, VSC induces drastic changes in the fluorescence spectrum of PE2, confirming that the self-assembled structure has a different packing under strong coupling. It should be noted that the fluorescence spectrum is not modified by the thin Au film in the present experimental conditions which is why the off-resonance spectrum (Figure 3D) is identical to the emission outside a cavity (Figure S3C). Unlike the fluorescence spectrum, the absorption spectrum does not change much in the long wavelength region (Figure 3). It suggests that the modified emission might come from an excited state dimer or higher order assembly. Indeed, as shown below, the packing formed under on-resonance condition is very different as can be seen from electron microscopy images. It should be noted that PE1 shows no changes under identical VSC conditions as can be seen in the SI (Figure S1).

Next, scanning electron microscopy (SEM) was used to visualize the structural changes induced by VSC (Figure 4). Interestingly under cooperative VSC of PE2, mostly spherical structures are formed (Figure 4A, B) as is clearly visible in the sample whereas in the absence of strong coupling, the aggregation of PE2 resulted in the formation of 2D amorphous flakes (Figure 4 C, D). More example of such SEM images from different runs are given in the SI (Figure S2). Interestingly, the spherical structures are very large, ranging from 2 to 20 μm in diameter, and sparse, probably due to few nucleation events. They consist of an outer wall and a dense core

which scatters brightly in the SEM image, and these are separated by a dark zone suggesting much less material present. We verified that there are no chemical modifications in these aggregates by dissolving them and recovering the monomer mass-spectrum. The emission of the dissolved material also recovers to the original monomeric spectrum. As a control experiment, the aggregation experiments in a cell under similar conditions was also performed. The absorption, emission, and the structure of the aggregates are identical to that of off-resonance conditions as shown in the SI (Figure S3). All the above SEM images were taken with dry samples after opening the holder. It was checked that before opening, spherical structures were already present in the solution by using optical microscopy. An example of an optical image is given in the SI (Figure S4).

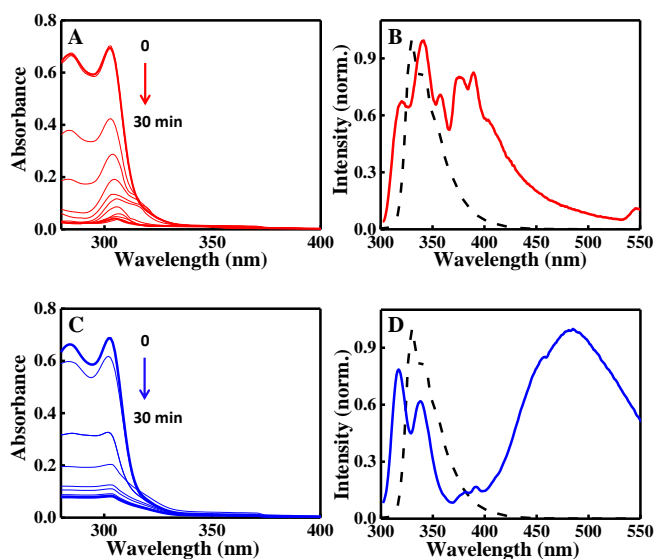


Figure 3: (A-D) Spectroscopic investigations of the self-assembly of PE2 molecules (1 mM in toluene, 23°C) under on-resonance (A,B) and off-resonance (C,D) conditions. Self-assembly of the PE2 molecule is monitored as a function of time by UV-visible absorption spectroscopy under VSC (A) and off-resonance (C) conditions (spectra are recorded every minute). The emission

spectra (B,D) of the PE2 monomer (black dashed line) and after aggregation in the presence (B, red trace) and absence (D, blue trace) of VSC.

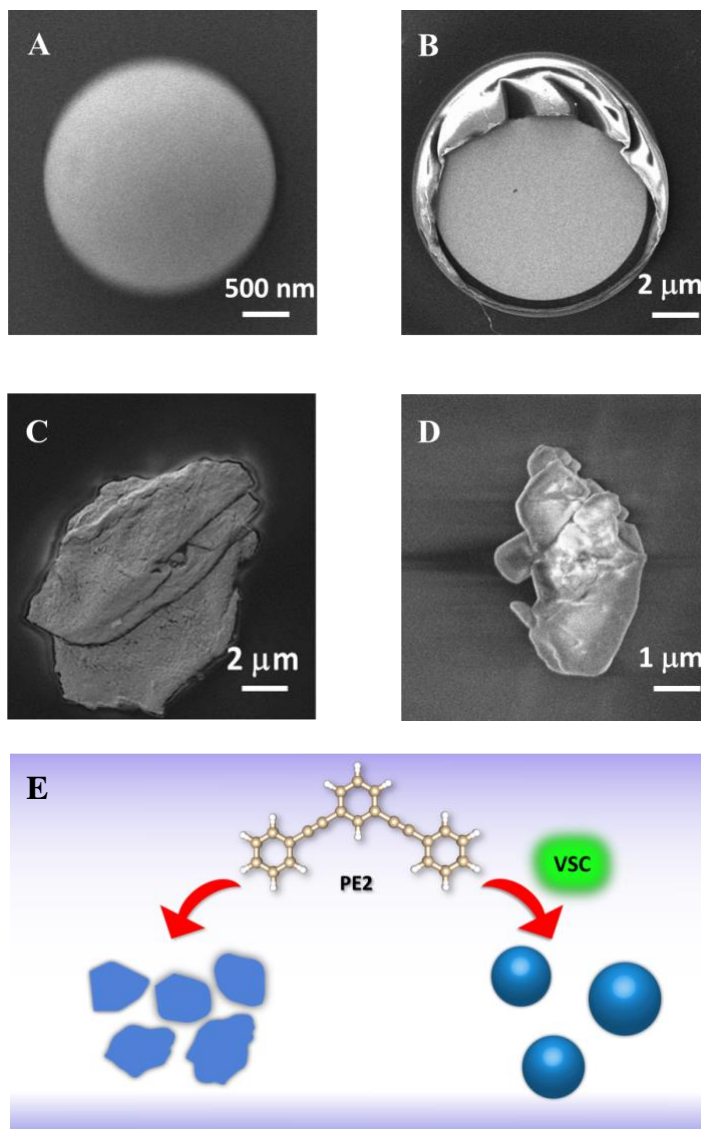


Figure 4: SEM images of the structures formed after the self-assembly of PE2 under VSC (A,B) and off-resonance (C,D) conditions. (E) Schematic representation of the formation of different self-assembled structures in the absence and presence of VSC.

We also analyzed the kinetics of aggregation carefully which involves a latency period after which the spectral changes become very significant (Figure 3) and follow a pseudo-first order

rate. This process under VSC is found to be slightly faster (0.39 min^{-1}) than that of the off-resonance (0.35 min^{-1}) condition but not enough to draw any conclusions (SI, Figure S5). Obviously, the aggregation process is complex and VSC might not affect significantly the rate limiting step even if it modifies the intermolecular interactions. Nevertheless, the slightly faster rate of aggregation under VSC will favor the formation of isotropic structures such as those observed. In another experiment, the aromatic C-H stretching band at 3027 cm^{-1} of PE2 was also cooperatively coupled with toluene (see Figure S6 in the SI) but in this case, VSC had no effect on the aggregation, resulting in the formation of amorphous flakes as in the absence of strong coupling. Finally, as shown in SI, cooperative VSC of PE1, the linear isomer, resulted in no change in the spectroscopic data nor in the structural features of the aggregates.

Considering all the above results, it is clear that the modifications induced by VSC are sensitive to both the type of vibration that is coupled and to the structural features of the isomers. PE1 and PE2 have different symmetry and as a consequence the polarity of PE2 (C_{2v} point group) is higher than the centrosymmetric PE1 ($D_{\infty h}$) which should make it more sensitive to any changes in the polarity or polarizability induced by VSC on the solvent and/or the solute.^{44, 48} After all, symmetry is clearly a key parameter that influences the effects of VSC.^{42,43} The fact that coupling the C-H stretching mode has no observable consequences while the C=C band of PE2 does strongly influence the aggregation process, is also reasonable when one considers the role of π - π interactions in the self-assembly of such aromatic molecules. Furthermore, π - π interactions are due to London-type dispersive forces that are sensitive to the electromagnetic fluctuations that pervade the universe and which are involved in the strong coupling process with the cavity mode. Finally, it should be recalled that the cooperative coupling is a collective phenomenon that leads

to the formation of collective states that potentially extend over the volume of the optical mode.¹⁷

¹⁸ This might also favor the self-assembly process.

In conclusion, the effect of VSC on modification of the self-assembly of aromatic molecules reveal that strong coupling can perturb the π - π interactions and thereby drive the system to a different structural minimum in the potential energy landscape. This confirms that VSC is a new tool to control self-assembly of molecules and more broadly to manipulate supramolecular chemistry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/XXXX>

Synthesis and characterization of PE1 and PE2, fabrication of the FP cavity, cavity tuning, self-assembly of PE1, SEM images of the PE2 aggregates, cell experiments, optical microscopy images, kinetics of self-assembly, and the self-assembly of PE2 under cooperative coupling of C-H bonds.

AUTHOR INFORMATION

Corresponding Authors

K. George Thomas - School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram (IISER-TVM), Vithura 695 551, India; <https://orcid.org/0000-0003-1279-308X>; E-mail: kgt@iisertvm.ac.in

Thomas W. Ebbesen - University of Strasbourg, CNRS, ISIS & icFRC, 8 allée Gaspard Monge, 67000 Strasbourg, France; <https://orcid.org/0000-0002-3999-1636>; E-mail: ebbesen@unistra.fr

Authors

Kulangara Sandeep - University of Strasbourg, CNRS, ISIS & icFRC, 8 allée Gaspard Monge, 67000 Strasbourg, France; <https://orcid.org/0000-0002-4275-3495>.

Kripa Joseph - University of Strasbourg, CNRS, ISIS & icFRC, 8 allée Gaspard Monge, 67000 Strasbourg, France.

Jérôme Gautier - University of Strasbourg, CNRS, ISIS & icFRC, 8 allée Gaspard Monge, 67000 Strasbourg, France.

Kalaivanan Nagarajan - University of Strasbourg, CNRS, ISIS & icFRC, 8 allée Gaspard Monge, 67000 Strasbourg, France; <https://orcid.org/0000-0002-2933-9951>.

Meleppatt Sujith - School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram (IISER-TVM), Vithura 695 551, India.

Notes

The authors declare no competing financial interest.

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