

Monomers That Form Conducting Polymers as Structure-Directing Agents: Synthesis of Microporous Molecular Sieves Encapsulating Poly-*para*-phenylenevinylene

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Abstract: We have developed a novel concept that uses monomers required for making conducting polymers as organic structure-directing agents, for the synthesis of microporous molecular sieves. We show that these monomers facilitate the formation of crystalline and amorphous molecular sieves depending on the synthesis procedure. The monomers filling the pores of the silicates can be polymerized under cer-

tain conditions, resulting in a polymer immobilized and protected inside the matrix. The concept was exemplified with *para*-phenylenemethylene-bis(1-tetrahydrothiophenium) and *para*-phe-

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nylenemethylene-bis(trimethylammonium) that were used to template microporous molecular sieves and subsequently to obtain poly-*para*-phenylenevinylene (PPV) inside the matrix. The organic self-assembled organic-inorganic material was extensively characterized and the implication on electrical conductivity is presented.

Introduction

The concept of templation and the use of structure-directing agents (SDA) to obtain micro- or mesoporous solids has been one of the major breakthroughs in material science.^[1] The crucial features are the self-assembly of the organic template, and the formation of the growing oligo/polymeric structures of the inorganic material.^[2,3]

However, in spite of the numerous uses of SDA for the synthesis of porous materials, a strategy in which the SDA, in addition to producing templation of the inorganic porous material, can have a special reactivity in the final material has been rarely exploited.^[4] In particular, the possibility that

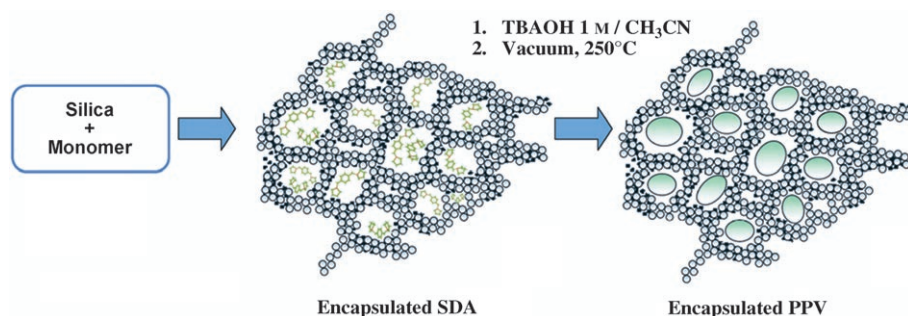
the initial SDA undergoes a polymerization after entrapment to give a functional polymer has, as far as we know, never been reported.^[5,6]

Conducting organic polymers and, specifically, those having a *para*-phenylenevinylene (PPV) structure have many interesting properties, such as electric conductivity, charge storage capacity, electrochromism, photovoltaic activity, and electroluminescence.^[5,7,8] One of the major drawbacks of most conducting polymers, and PPV in particular, is the high tendency to undergo degradation due to the oxidative degradation of their π conjugation.^[9–14] Exposure of the conducting polymer to oxygen, moisture, and other nucleophiles must be avoided to minimize degradation and increase operation lifetime. In this context, it has been reported that PPV can be obtained inside aluminosilicates by adsorbing the monomer on a preformed porous material and effecting the polymerization under basic conditions.^[15–17] The resulting encapsulated PPV exhibits a remarkable protection from photochemical degradation in the open atmosphere, whereas analogous treatment of pure PPV produces rapid degradation to a very large extent.^[9–14] However, PPV preparation inside the porous material was time-consuming, requiring the use of the performed microporous host and, then, four consecutive steps. Moreover, the loading of PPV inside the inorganic matrix was low (4–5 wt %).

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Herein we report that suitable PPV monomers can be used as SDAs for the preparation of microporous molecular-sieve silicates. After formation of the inorganic solid around the monomer, this can be transformed in some cases into PPV that remains entrapped inside the inorganic matrix. Scheme 1 illustrates the strategy based on the concept of using a reactive SDA to form an encapsulated polymer. The photochemical properties of the encapsulated polymer were determined by laser flash photolysis.

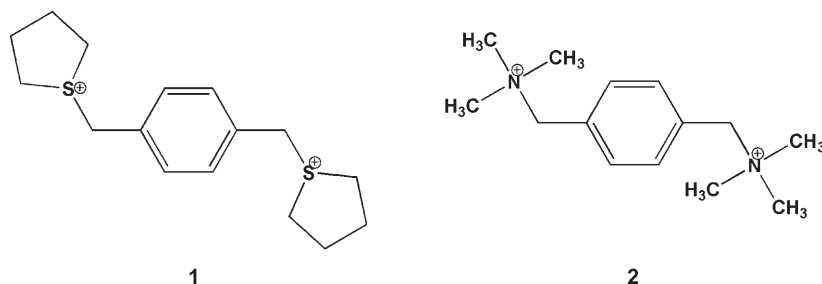


Scheme 1. Use of a SDA to template the formation of a microporous molecular sieve and the latter as a monomer to effect the formation of an encapsulated polymer inside the silica matrix.

Results and Discussion

In this work we have used two potential PPV monomers, namely *para*-phenylenemethylene-bis(1-tetrahydrothiophenium) (**1**) and *para*-phenylenemethylene-bis(trimethylammonium) (**2**), as SDAs for the preparation of silicates. To carry out the synthesis of a crystalline microporous silicate under hydrothermal conditions, we first studied the stability of these two molecules in basic aqueous media at 150 °C for 48 h. It was observed that although the bistrimethylammonium cation **2** was stable under these conditions, the bistetrahydrothiophenium **1** reacts giving rise to an insoluble, gummy polymeric material precursor of PPV. This instability to the hydrothermal conditions precluded the use of **1** for the synthesis of zeolitic materials under conventional conditions, but established the suitability of **2** as a SDA due to its stability to prolonged heating periods under basic conditions.

The use of **2** as a SDA under hydrothermal conditions by using tetraethylorthosilicate (TEOS) as source of silicon



leads to the crystallization of a solid, whose XRD pattern corresponds to a ZSM-12 zeolite. Figure 1 shows a representative XRD pattern of the solids obtained. According to chemical analysis and thermogravimetry, about 10 wt% of the solid corresponds to the SDA **2**. Molecular modeling (see Supporting Information Figure S1) shows the best docking of compound **2** inside the micropores of ZSM-12.

However, in spite of the large loading of monomer, all the efforts to promote the formation of PPV by in situ polymerization of encapsulated SDA **2** under basic conditions were unsuccessful. Following earlier successful procedures to obtain PPV inside zeolites X and Y,^[15,17] the zeolite was even exchanged with cesium acetate to introduce basic sites into the zeolite framework, but these cesium-exchanged samples also failed to form PPV. Molecular modeling of **2** within the pores of ZSM-12 show that this molecule is strongly constrained within the relatively rigid crys-

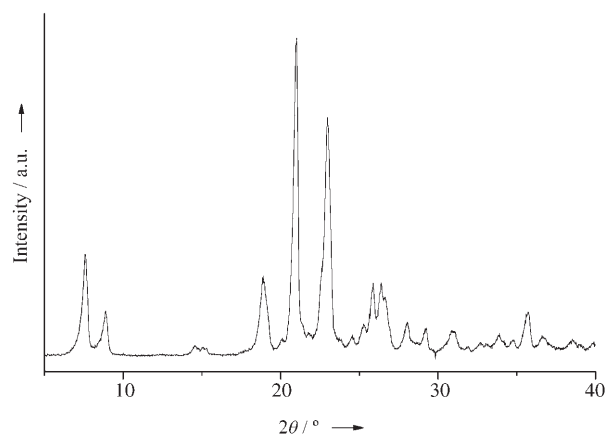
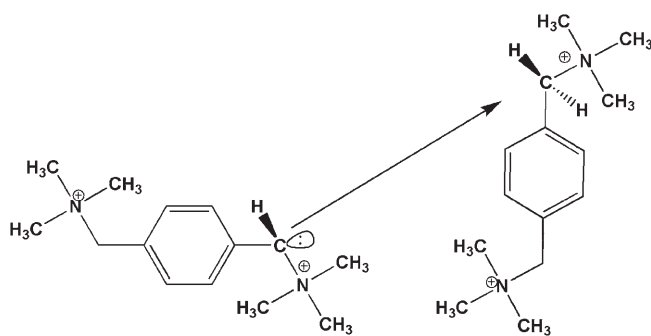


Figure 1. Representative XRD pattern of the solids obtained by using the quaternary ammonium cation **2** as SDA.

talline structure of the zeolite and the spatial restrictions of SDA **2** inside the channels impede monomer coupling that is a process requiring the nucleophilic attack of one monomer on another.^[18] Scheme 2 indicates the proposed rationalization for the failure of polymerization.

Considering that compound **1** is a more suitable precursor of PPV and that this compound is unstable to prolonged heating under basic conditions in



Scheme 2. Steric requirement for the nucleophilic attack of the zwitterionic nucleophile on a monomer leading to the formation of the polymeric backbone.

aqueous medium, and taking into account that polymerization should be facilitated by more-flexible inorganic structures, we carried out the synthesis of silicate at room temperature and neutral pH by using monomer **1** as the SDA. To do this, we used TEOS as a source of silica, and tromethamine and ethanolamine as mineralizing agents.^[19] This aminoalcohol can mimic silicatein α , a natural enzyme responsible for the formation of siliceous deposits in microorganisms.^[20] This synthesis procedure should produce a highly flexible amorphous structure with a narrow distribution of pores, which should be very suitable for molecular imprinting, particularly compared to rigid zeolites.^[19]

Working under these conditions, a material (**1**@mpSiO₂) containing **1** as a SDA was obtained. As expected, analogous **2**@mpSiO₂ material was also prepared by using compound **2** as the SDA. Elemental analysis, as well as IR and NMR spectroscopy (see Figures 2 and 3, respectively) show that the monomer **1** was intact within the synthesized material. Chemical analysis indicates that the loading of **1** in **1**@mpSiO₂ was 14 wt%, notably higher than the maximum loading that was achieved by adsorbing the same monomer **1** in preformed faujasites (5 wt%). In agreement with the above expectations, the material was amorphous to XRD and contained a large number of unconnectivities, that is, Q³

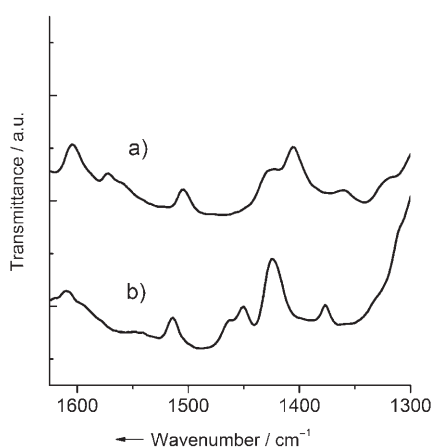


Figure 2. IR spectra of a) pure PPV and b) PPV@mpSiO₂ sample after outgassing at 100°C under 10⁻² Torr for 1 h.

Si(3Si)(1OH), and Q² Si(2Si)(2OH), as can be deduced from the ²⁹Si magic angle spinning (MAS) NMR spectrum (Supporting Information Figure S2). After calcination at 540°C to remove the organic structure-directing agent, the resultant material shows the porosity with a BET surface area of 433 m²g⁻¹ (Supporting Information Figure S3) and a pore-size distribution, measured by Ar adsorption, centered at 6.5 Å (Supporting Information Figure S3, inset).

From all the above information it can be concluded that upon performing the synthesis at room temperature and neutral pH by using a mimic of silicatein α for mobilizing the silica and monomers as SDA, a flexible amorphous material with a well-defined pore-size distribution in which the unmodified monomer is included was obtained. The following challenge was to achieve the polymerization of the monomer. Thus, after treating the sample **1**@mpSiO₂ with 1-M solution of tetrabutylammonium hydroxide (TBAOH) in acetonitrile^[21–23] and heating the dry powder at 250°C under 0.1 Torr for 4 h, the solid turns bright yellow. This visual change is generally a sign of the successful polymerization and formation of PPV. In optical spectroscopy, the appearance of a band having an onset in the visible region at 400 nm that is absent in the monomer or in the silicate is observed (Supporting Information Figure S4). This absorption band is characteristic of the PPV polymer. This could be confirmed by comparing the IR spectra of the solid resulting after the polymerization treatment (PPV@mpSiO₂) with those previously reported for this polymer (see Figure 2). The IR spectra show peaks at 1620 and 1500 cm⁻¹ corresponding to the conjugated C=C double bonds and the aromatic stretching vibrations, respectively. The other bands in the IR spectrum taken as a fingerprint also coincide with PPV.^[21–23]

To show that the polymerization occurs inside of the pores of the microporous materials, some gas-adsorption experiments with N₂ were performed (Supporting Information Figure S5). Results of the first experiment show that the monomer is completely filling the microporous matrix as the SDA before the polymerization, because the N₂-adsorption curve for the as-prepared **1**@mpSiO₂ sample gives no microporosity, with a BET surface area of 3 m²g⁻¹. Then, polymerization of the monomer inside the pores was performed. The isotherm of PPV@mpSiO₂ shows again no microporosity, with an area BET of 2 m²g⁻¹. Moreover, chemical analysis for two samples shows that the C content is maintained before (9.6 wt% C) and after (9.2 wt% C) polymerization. Finally, to demonstrate the advantage of the herein-reported synthesis methodology for the polymerization versus the conventional impregnation process, a pure silica Beta zeolite that presents a micropore volume similar to that of our microporous material, was selected and impregnated with the same content of PPV. The N₂-adsorption measurement (PPV-Beta) shows clearly that the polymer is not filling the Beta pores.

Solid-state MAS ¹³C NMR of PPV@mpSiO₂ (Figure 3) also confirmed the success of the polymerization. In particular, the disappearance of the aliphatic peaks corresponding

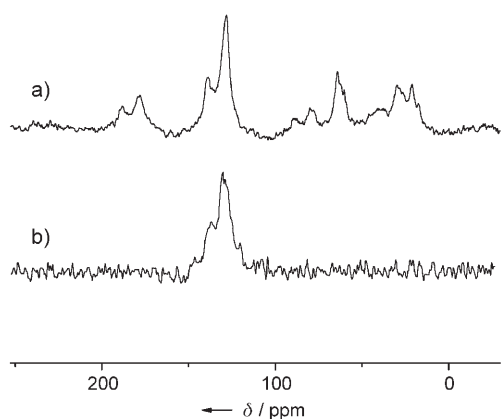


Figure 3. Solid-state ^{13}C NMR spectrum of a) $1@mp\text{SiO}_2$ and b) $\text{PPV}@mp\text{SiO}_2$.

to the tetrahydrothiophenium ring and the methylene carbon after the polymerization is a sign of the elimination of this residue and the formation of C=C double bonds. In accordance with this, only sp^2 carbons are recorded in the ^{13}C NMR spectrum of $\text{PPV}@mp\text{SiO}_2$.

One remarkable property of PPV, which is the base for its application in electroluminescence, is its intense emission.^[22] As expected, upon excitation at 400 nm $\text{PPV}@mp\text{SiO}_2$ exhibits a strong, structured fluorescence at $\lambda_{\text{em}} = 490$ nm. Figure 4 shows the fluorescence and the corresponding exci-

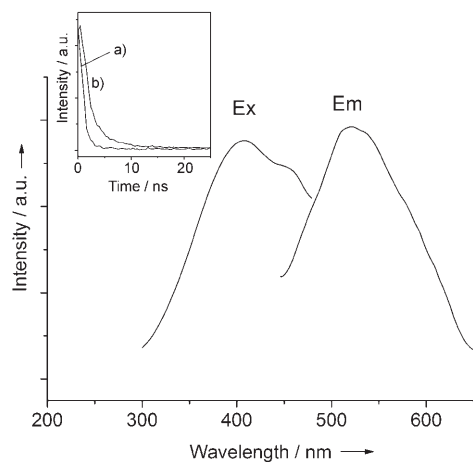


Figure 4. Emission spectra (Em, $\lambda_{\text{ex}} = 370$ nm) and excitation spectra (Ex, $\lambda_{\text{em}} = 530$ nm) of $\text{PPV}@mp\text{SiO}_2$. The inset shows a) the temporal profile of the emission and b) the blank signal of the lamp.

tation spectra. The temporal profile of the emission fits monoexponential kinetics with a τ value of 2 ns, a common value for the fluorescence half-life of PPV.

Laser flash photolysis of $\text{PPV}@mp\text{SiO}_2$ was performed to determine the photoactivity of the material and the nature of the transients involved. Upon 355 nm laser excitation a broad band spanning from 450 to 800 nm decaying in the microsecond timescale was recorded. The spectrum exhibits a negative signal below 400 nm that corresponds to the

bleaching and recovery of the PPV ground state. Extended exposure of the sample to the laser flash did not lead to spectroscopic changes, indicating the photochemical excitation does not produce decomposition of the sample and formation of permanent products. In contrast, analogous treatment of pure PPV film led to degradation of the polymer that could be observed visually.

The lack of coincidence of the temporal decays measured at different wavelengths indicates that most probably this broad band corresponds to several transient species, making an exact kinetic analysis of the transient spectra difficult. Nevertheless, the temporal profiles of the signal above 600 nm were identical with a half-life determined by fitting the decay of the signals to a first-order kinetics of 50 μs . Figure 5 shows the spectrum and signal decays to illustrate the previous points.

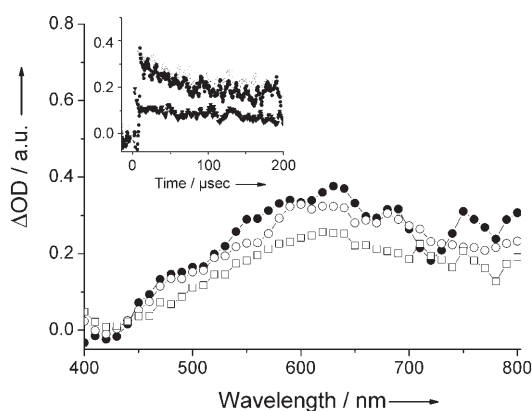


Figure 5. Transient spectra recorded after 20 (\bullet), 50 (\circ), and 100 (\square) μs after 355-nm laser excitation. The inset shows the temporal decays at 500 (\blacktriangledown), 600 (\circ), and 700 nm (\bullet).

Concerning the nature of the transient, we suggest that the absorption from 600 to 800 nm and beyond corresponds to ejected electrons. This proposal is based on the similarity of this UV/Vis spectrum with other transient spectra previously reported for electrons in silicates.^[24] The lifetime, which is in the range of the values previously measured for photoejected electrons, and results of the quenching experiments support this assignment. Thus, the signal in this region was not affected by the presence of triplet quenchers (oxygen) or hole quenchers (methanol), whereas addition of nitromethane (strong electron acceptor) accelerates the decay.

Detection of electrons decaying in the submillisecond timescale upon photoexcitation is relevant in the context of many applications of PPV, such as charge transport and electroluminescence. In the latter, holes and electrons should migrate to the working electrodes and recombine in the PPV layer generating an electronic excited state. Our transient spectra show that electrons and holes can also be formed photochemically.

To explore if the presence of incorporated conducting polymer in PPV@mpSiO₂ is manifested in some properties of the solid, we proceeded to determine the electrical conductivity. Figure 6 shows a comparison of the current versus voltage (*I/V*) profiles for PPV@mpSiO₂ and 1@mpSiO₂ leaching conducting polymer. The electrical conductivity experiences a dramatic enhancement due to the presence of the incorporated conducting polymer.

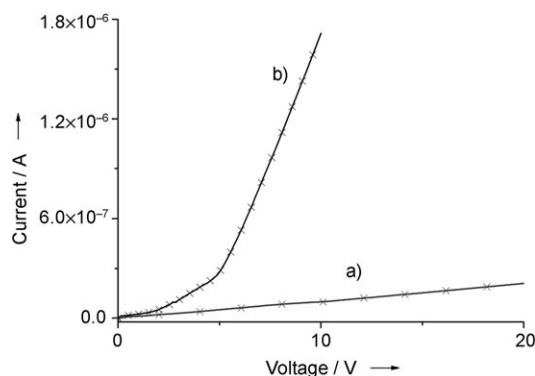


Figure 6. Curve of *I/V* of 1@mpSiO₂ a) before and b) after the polymerization.

Conclusion

We have shown that organic SDAs can serve not only to impart the tridirectional porosity of porous solids, but they can also be designed to be transformed into the desired guest. More specifically, monomers of PPV can facilitate the formation of crystalline or amorphous molecular sieves depending on synthesis conditions. By taking advantage of a novel sol-gel procedure that allows the synthesis of molecular sieves at room temperature and neutral pH, the proposed methodology can be general and implemented to pH- and temperature-unstable SDA monomers, as in the case of monomer 1. Thus, we have shown that the most relevant conducting polymer PPV can be obtained embedded in a solid whose pore system is especially suited to host the monomer. Preliminary tests show that the resulting material exhibits properties imparted by the conducting polymer.

Experimental Section

Synthesis procedure of ZSM-12 using compound 2 as SDA: A pure silica ZSM-12 sample was prepared starting from a gel with the following molar composition: SiO₂:0.20 C₂₀H₃₈N₂(OH)₂:0.40 HF:7 H₂O in which C₂₀H₃₈N₂(OH)₂ is 1,4-bis(triethylammoniummethyl)benzene hydroxide. The preparation method is as follows: First, tetraethylorthosilicate (TEOS) (19.42 g) was hydrolyzed in a solution of 1,4-bis(triethylammoniummethyl)benzene hydroxide (22.83 g, 0.876 M) and was left under stirring until the ethanol formed completely evaporated and the amount of water was necessary to reach the final composition. Then, HF (0.83 g, 48% wt in water) was added and the mixture was homogenized. After 7 days of crystallization at 448 K in polytetrafluoroethylene (PTFE)-lined stainless-steel autoclaves, a powder was obtained that after washing and

drying at 373 K yields a material whose X-ray diffraction (XRD) pattern closely corresponds to that reported for ZSM-12 zeolite.^[25]

Synthesis of 1@mpSiO₂ and 2@mpSiO₂: The material preparation was carried out at RT and neutral pH with the following composition: Si(OEt)₄:0.2 tromethamine:0.05 ethanolamine:0.25 PPV monomer:12 H₂O. Synthesis gel was prepared at RT (300 K) in polypropylene screw-cap containers (50 mL). In the preparation, Trizma hydrochloride buffer solution 11-M, pH 7.0 (4.79 g, Sigma-Aldrich) containing the tromethamine was added first. Then, PPV monomer, bromide (2.2 g), and tetraethylorthosilicate (4.17 g, Merck) were also added to the container under magnetic stirring. Finally, ethanolamine (312 mg, Sigma-Aldrich, >98%) was incorporated into the mixture. The solid was filtered, washed, and dried at room temperature after one week of stirring.

Synthesis procedure of PPV@mpSiO₂: Polymerization of the PPV monomer inside the pore system of the amorphous siliceous host was achieved by basic treatment of the solid with tetrabutylammonium hydroxide (TBAOH), as adapted from already published methodologies.^[26] Briefly, the solid sample (100 mg) was submitted to thermal treatment at 100°C under reduced pressure to eliminate adsorbed water, and was then purged with dry nitrogen. To this solid, a 1-M TBAOH solution in acetonitrile was added and the slurry was stirred overnight at room temperature and under nitrogen atmosphere. The aim of this treatment is to substitute (some of) the hydroxy groups of the material. The TBAOH solution was filtered off and the solid was heated overnight under vacuum at 250°C, which caused a color change of the powder from white to yellow.

Laser flash photolysis measurements: The laser flash photolysis experiments were carried out by using the third (355 nm) harmonic of a Q-switched Nd:YAG laser (Spectron Laser Systems, UK; pulse width ca. 9 ns and 20 mJ pulse⁻¹). The signal from the monochromator/photomultiplier detection system was captured by using a Tektronix TDS640A digitizer and transferred to a PC computer that controlled the experiment and provided suitable processing and data-storage capabilities.

Conductivity measurements: Measurements of the electrical conductivity were carried out in a cell having aluminum as cathode and a transparent conductive indium tin oxide (ITO) surface on a glass substrate as anode. A schematic of the electronic system used to determine the electrical conductivity is shown in the Supporting Information Figure S6. Measurements were carried out by using ambient-equilibrated zeolite powders deposited as self-supported dry thin films of 50 μm. Figure S6 shows a schematic of the cells being used.

Characterization techniques: Solid-state ¹³C NMR spectra were recorded by using a Varian 400 MHz at a spinning rate of 5.5 kHz. Ground-state diffuse reflectance UV/Vis spectra were recorded by using a Cary 5G using a praying mantis accessory for solids and using BaSO₄ as standard. FTIR spectra were recorded by using a Nicolet Impact 410 spectrophotometer using KBr disks or self-supported wafers compressed to 2 Ton cm⁻² for 2 min. Photoluminescence measurements were performed at room temperature in N₂-purged septum-capped quartz cells in an Edinburgh FL3000 spectrofluorometer using a Xe-doped mercury lamp and a Czerny-Turner monochromator.

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