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Keywords: silicene; silicon; Raman; STM; epitaxial growth; oxidation
Abstract: We report the growth of Si nanostructures, either as thin films or nanoparticles, on graphene substrates. The Si nanostructures are shown to be single crystalline, air stable and oxidation resistive, as indicated by the observation of a single crystalline Si Raman mode at around 520 cm–1, a STM image of an ordered surface structure under ambient condition, and a Schottky junction with graphite. Ultra-thin silicon regions exhibit silicene-like behavior, including a Raman mode at around 550 cm–1, a triangular lattice structure in STM that has distinctly different lattice spacing from that of either graphene or thicker Si, and metallic conductivity of up to 500 times higher than that of graphite. This work suggests a bottom-up approach to forming a Si nanostructure array on a large-scale patterned graphene substrate that can be used to fabricate nanoscale Si electronic devices.
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Keywords: organic?inorganic hybrids long-term stability structural ordering optical properties degradation mechanism
Abstract: Organic–inorganic hybrids may offer material properties not available from their inorganic components. However, they are typically less stable and disordered. Long-term stability study of the hybrid materials, over the anticipated lifespan of a real-world electronic device, is practically nonexistent. Disordering, prevalent in most nanostructure assemblies, is a prominent adversary to quantum coherence. A family of perfectly ordered II–VI-based hybrid nanostructures has been shown to possess many unusual properties and potential applications. Here, using a prototype structure ?-ZnTe(en)0.5—a hybrid superlattice—and applying an array of optical, structural, surface, thermal, and electrical characterization techniques, in conjunction with density-functional theory calculations, we have performed a comprehensive and correlative study of the crystalline quality, structural degradation, electronic, optical, and transport properties on samples from over 15 years old to the recently ...
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Partners

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I certify that the information in the report is complete and accurate:
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Project title:

Excitons and exciton-polaritons in novel organic-inorganic hybrids with sub-nano II-VI or III-V layers

PIs: Yong Zhang (Bissell Distinguished Professor, Electrical and Computer Engineering Department) and **Thomas A. Schmedake** (Professor, Chemistry Department)

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1. Introduction

The project "Excitons and exciton-polaritons in novel organic-inorganic hybrids with sub-nano II-VI or III-V layers" ran from Feb. 15, 2018 to Feb. 14, 2021, with no-cost-extension to Sept. 30, 2021. The program supported 2 PIs (partial summer time) along with 4 PhD students and 1 MS student for various lengths of time, on a total budget of $ 399,381.

The team published one peer-reviewed paper (ACS Nano) [1], has one brief review paper under review (J. Lumin.), and two manuscript under preparation, with direct acknowledgement of the support from this award. The team members gave multiple international conference/workshop presentations, including three keynote/invited talks and two oral presentations (OPTICSMEET2021, ICL 2020 (held in 2021), Vebleo 2020, ICCES 2019, II-VI workshop 2021, APS 2019).

The project was motivated by the earlier work of the lead PI and his collaborators that reported the discovery of a new family of II-VI based organic-inorganic hybrid nanostructures [2] and findings of a few interesting and unique properties from a few prototype structures [3, 4].

II-VI based organic-inorganic hybrid structures were first reported in 2000 for three structures: α-ZnTe(en)$_{0.5}$, β-ZnTe(en)$_{0.5}$, and α-ZnTe(pda)$_{0.5}$, with their crystal structures determined and optical bandgap estimated [5]. Thereafter, many more II-VI hybrids with group II elements Zn, Cd, and Mn and group VI elements S, Se, and Te have been synthesized, with their structure being analyzed, and optical bandgaps estimated [2, 6, 7]. These hybrid structures can be categorized into three groups [2]: as shown schematically in Figure 1(a), (1) three-dimension (3D) like structures, 3D-(MQ)L$_{0.5}$, where two-monolayer thick (110) slabs of a zinc-blende structure (β phase) or their wurtzite equivalences (α phase) are interconnected by small organic molecules, for instance, ethylenediamine (en) = $C_2N_2H_8$. (2) Two-dimension (2D) like structures, 2D-(MQ)L, where only one end of the organic molecule bonds to the inorganic layer of the same thickness as in the 3D structure, resembling layered structures. In this group, it is also possible to have structures with the inorganic slab thickness doubled, 2D-(M_2Q_2)L [8]. (3) One-dimension (1D) like structures, where the single atom thick binary chains of the wurtzite structure bond with the molecules to only one end for each molecule, and an assembly of such quasi 1D structures in parallel forms the hybrid crystal. The individual inorganic chains in these 1D structures can be viewed as the smallest quantum wire practically possible. The array has a very high density around $2x10^{14}$ wires/cm^2 for 1D-ZnTe(pda). Fig. 1(b) compares three ZnTe based hybrid structures, 3D-β-ZnTe(en)$_{0.5}$, 2D-ZnTe(N_2H_4), and 1D-ZnTe(pda), as examples for 3D, 2D, and 1D structures, respectively [2].

Limited early efforts on selected structures had shown that the II-VI based hybrid structures were rather unique in a number of ways not only within the organic-inorganic hybrid materials but also in general semiconductor materials. Almost any property being investigated, something unusual was observed. For instance, a superlattice like 3D hybrid β-ZnTe(en)$_{0.5}$ showed a large bandgap shift from 2.3805 eV of ZnTe to 3.7192 eV (at 1.5 K), accompanying by strong band edge excitonic absorption up to around 1,100,000 cm^{-1} [3]. Compared to 140,000 cm^{-1} for ZnTe, this is likely the strongest band-edge excitonic absorption in semiconductors. Due to the strong quantum and dielectric confinement, a large exciton binding energy over 200 meV was predicted and band-edge excitonic emission was observed at 300 K [3]. This particular structure was also predicted to be a suitable candidate for p-type transparent conducting application [3]. The structure was further shown to exhibit broad temperature range (4 – 400 K) zero-thermal expansion along the organic-inorganic stacking direction [4], which is likely the first non-oxide semiconductors showing zero

thermal expansion. These exciting observations and predications have motivated us re-engaging the exploration of the II-VI based hybrids, particularly under the context of strong current interest in organic-inorganic hybrid halide perovskites. Despite the impressive performance in PV application, the hybrid halide perovskites are known to have poor stability under ambient conditions. The II-VI hybrids offer great opportunities to explore hybrids beyond halide perovskites.

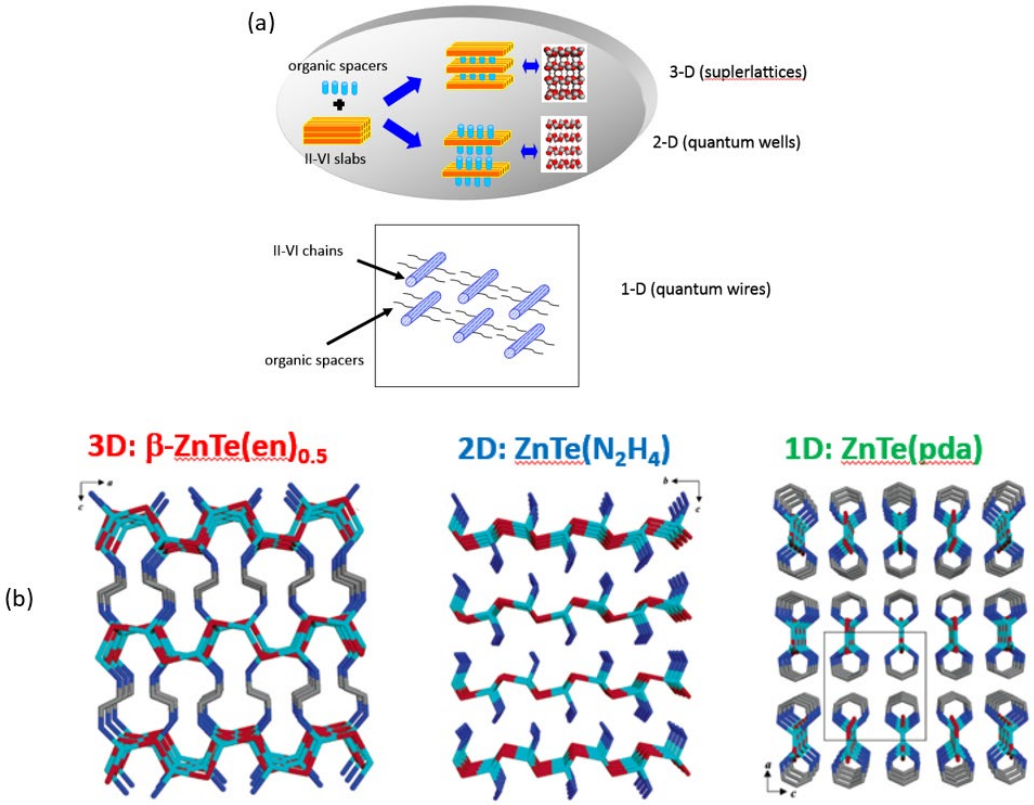

Fig. 1. (a) Schematics of II-VI based hybrids in 3D, 2D, and 1D structures. (b) Crystal structures of prototype 3D, 2D, and 1D structures based on ZnTe.

The general goal of this project was to investigate the quantum effects of excitons and exciton-polaritons in II-VI and III-V sub-nano scale organic-inorganic hybrids (focusing on the "3D" structures). The specific tasks proposed were

1) Understand how the variations in organic spacer and chalcogen element affect the excitonic effects in the "3-D" inorganic-organic materials to achieve the tuning of physical properties from 2-D to 3-D behavior.
2) Success in synthesis control to obtain larger hybrid crystals (at least 10 μm in dimension) to satisfy the requirements for more sophisticated optical characterization and device fabrication needs.
3) Success in doping hybrid structures.
4) Success in making III-V based hybrid structures.

2. Accomplishments

(a) Proposed tasks

Taking 3D-(MQ)$L_{0.5}$ as a prototype structure, selecting MQ = ZnTe, and L = $C_nN_2H_{2n+4}$ (n = 0, 2-5), one can achieve a single atomic level control on the thickness of the organic spacer layer by changing the number of C atoms. Previous studies mostly focused on the β phase of n = 2 or L = $C_2N_2H_8$ (ethylenediamine) [3, 4]. In this project, we have synthesized 3D-ZnTe$(L)_{0.5}$ with n = 2 – 4. For n = 2, both α and β phase have been obtained; for other n values, only the α phases have been reported [2]. Figure 2 and Figure 3 show, respectively, their PL and Raman spectra at 300 K. For n = 2, the bandgap of the α phase (~3.768 eV) is somewhat higher than that of the β phase (~3.556 eV), as expected [2, 3]. It is also unsurprised that the n = 3 structure α-ZnTe$(pda)_{0.5}$ shows a lower PL energy due to increased spacer or barrier layer thickness (E_g ~ 3.294 eV). However, it is puzzling why no PL was observed for n = 4 structure α-ZnTe$(bda)_{0.5}$, while its Raman spectrum seems to indicate that the sample had high crystal quality. Clearly, these hybrids are distinctly different in structure and optical property with changing the spacer thickness one C at a time! However, these materials have not yet been systematically characterized, and electronic structure modeling should also be performed for them.

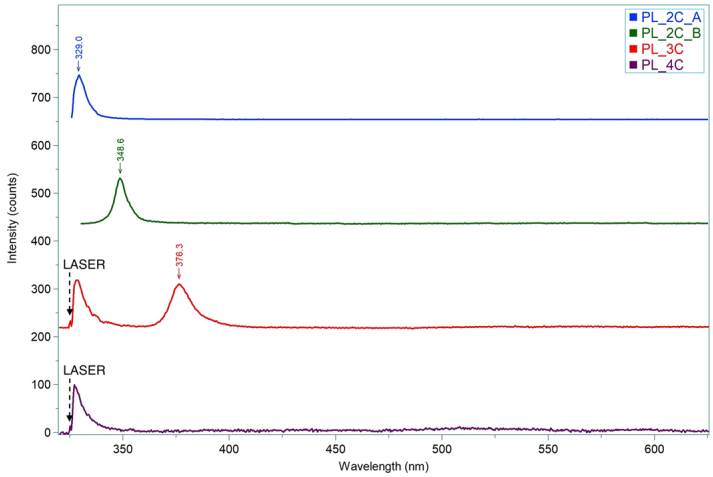

Fig. 2. Room temperature PL spectra of 3D-ZnTe$(L)_{0.5}$ with n = 2 – 4 excited by 325 nm laser.

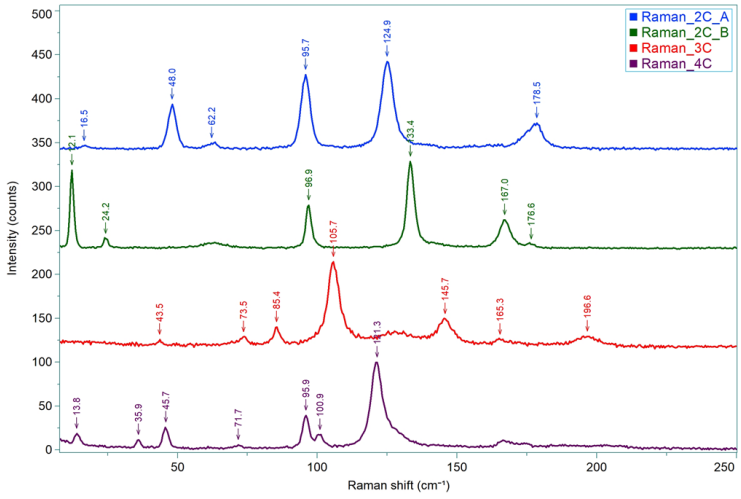

Fig. 3. Room temperature Raman spectra of 3D-ZnTe$(L)_{0.5}$ with n = 2 – 4 excited by 532 nm laser.

We also attempted to dope α- and β-ZnTe(en)$_{0.5}$ with Cu and Ag, which are known to behave as p-type dopants in ZnTe. ToF-SIMS mapping was used to probe the dopant incorporation. Figure 4 shows that Ag is indeed present in a β-ZnTe(en)$_{0.5}$ crystal. The two lower right panels are the spatial maps at two Ag isotope masses (107 and 109), compared to the upper right panels for two Zn isotope masses (64 and 66). The two Ag isotope maps confirm the incorporation of Ag, although the distribution is not uniform. Figure 5 shows the spatial maps of Cu (mass 63) and two Zn isotopes in Cu-doped α- and β-ZnTe(en)$_{0.5}$. In these samples, the dopant distributions are more uniform. The electrical properties of these doped samples are yet to be characterized.

Because of the constrain of resources, we did not attempt to synthesize the III-V based hybrids.

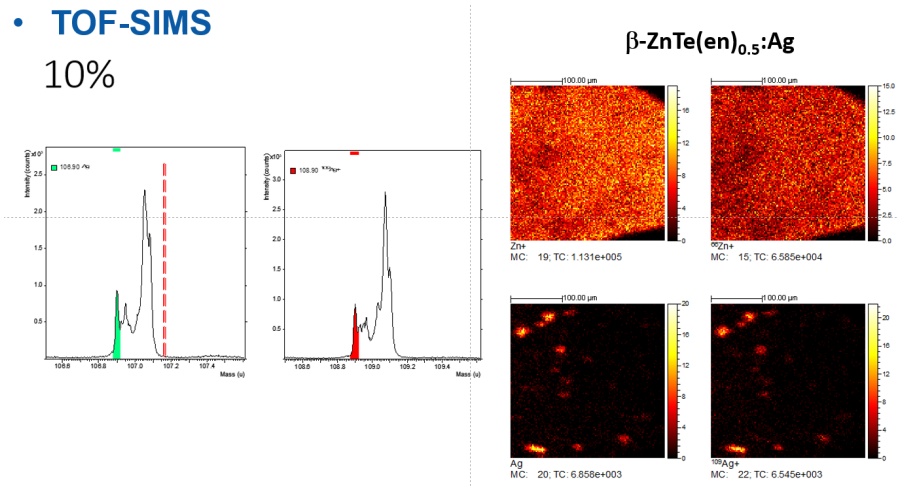

Fig. 4. TOF-SIMS spatial mapping results of Ag-doped β-ZnTe(en)$_{0.5}$ crystal.

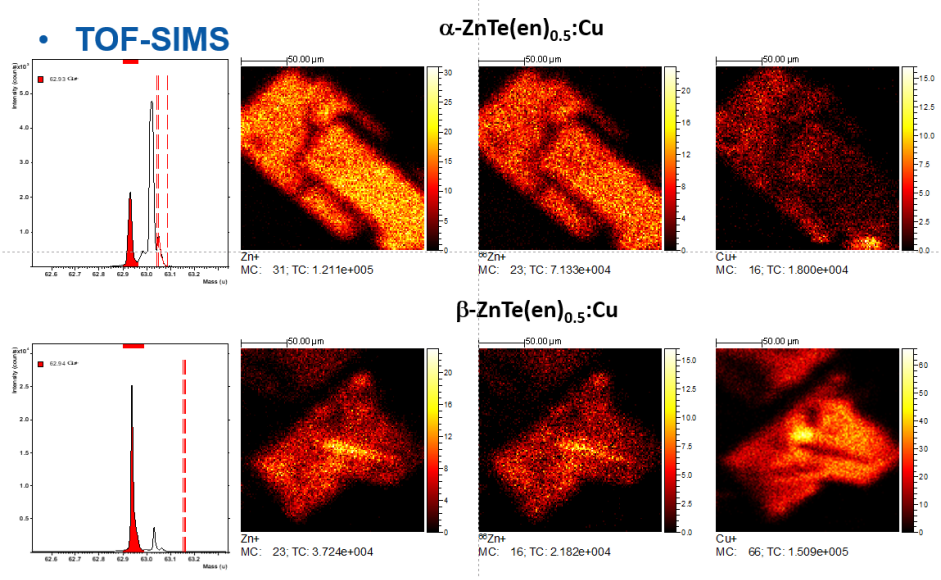

Fig. 5. TOF-SIMS spatial mapping results of Cu-doped α- and β-ZnTe(en)$_{0.5}$ crystal.

(b) Comprehensive studies on β-ZnTe(en)$_{0.5}$

To our surprise, at the beginning of the project, we found that some of the over-one-decade old hybrid samples, studied by the lead PI while at NREL between around 2003 – 2008, remained nearly the same as the newly made samples, although some others had degraded to varying degrees. Given the fact that the hybrid halide perovskites, even though the stability has been substantially improved compared to a few years back, still could not last for more than a few months, the II-VI based hybrid β-ZnTe(en)$_{0.5}$ offered a unique opportunity to investigate the fundamental science questions regarding the long-term stability of hybrid materials.

We also noted that β-ZnTe(en)$_{0.5}$ seemed to exhibit very high degree of structural ordering, manifested as very small Raman linewidths [2] and XRD linewidths [4], comparable to many III-V and II-VI binaries, which is rather unusual for such a complex structure (with 32 atoms/unit cell). In fact, mot hybrid materials, including those hybrid halide perovskites [9], are structurally disordered. Based on our past experience, we were also aware of that most inorganic superlattices, such as GaAs/AlAs [10], InAs/GaSb [11], InAs/InAsSb [12], always exhibited significant level of layer width fluctuation and atomic interdiffusion at the interface. This point concerns macroscopic scale structural ordering, which can be probed by a macroscopic scale characterization technique, such as XRD. Furthermore, even the best available semiconductors such as GaAs, CdTe, $MAPbI_3$, seemed to have considerable amount of SRH type point defects that typically diminished the PL quantum efficiency at low excitation density [9]. This point concerns the microscopic scale structural ordering.

Therefore, we decided to seize the opportunity to address the relevant questions below using β-ZnTe(en)$_{0.5}$ as the prototype structure:

1) What are the intrinsic mechanisms that dictate the long-term stability of a hybrid material?
2) What are the extrinsic mechanisms that may affect the long-term stability of a hybrid material?
3) How can we make a perfect heterostructure (i.e., free of atomic interdiffusion and layer width fluctuation)?
4) How can we suppress the point defects in a "bulk" material?

To this end, we have performed a comprehensive and correlative study of the crystalline quality, structural degradation, electronic, optical, and transport properties on samples from over 15 years old to the recently synthesized [1]. We have found that some of the over 15-year-old samples remain as good in structure and property as freshly made ones, which is perhaps the first report of hybrid materials with documented long-term stability that is expected for most electronic devices. The findings show that they exhibit an exceptionally high level of crystallinity not only in macroscopic scale, manifested as very small XRD rocking curve and 2θ scan linewidths (20-30"); but also, in microscopic scale, manifested as almost no below bandgap emission other than the band edge excitonic emission in room temperature PL and linear PL intensity vs. excitation density over 6 orders in magnitude (implying minimal amount of SRH centers [9]).

This study reveals (1) what level of structural perfectness is practically achievable in a complex organic–inorganic hybrid structure or a man-made superlattice in general, suggesting a non-traditional strategy to make periodically stacked heterostructures with abrupt interfaces and a 3D volume with minimum point defects; and (2) how the stability of a hybrid material is

affected differently by its intrinsic attributes, primarily formation energy and kinetic barrier, and extrinsic factors, such as surface and defects. By correlating the rarely found long-term stability with the calculated relatively large formation energy of β-ZnTe(en)$_{0.5}$, using a density-functional theory, and contrasting with the case of hybrid perovskite, this work illustrates that formation energy can serve as an effective screening parameter for the long-term stability potential of hybrid materials. The results of the prototype II–VI hybrid structures will, on one hand, inspire directions for future exploration of the hybrid materials, and, on the other hand, provide metrics for assessing the structural perfectness and long-term stability of the hybrid materials.

3. Perspectives

What has been explored so far on these II-VI based hybrids is only the tip of iceberg of the rich science and potential in applications. Here we would like to mention a few possible areas that we believe to be of great interest in the future study:

1) **Unusual elastic properties** Elastic constants C_{ij} of β-ZnTe(en)$_{0.5}$ have been calculated using density-functional theory (DFT) [13]. The elastic response of the hybrid is unsurprised to be highly anisotropic. For instance, if (x,y,z) is assumed to match the (*b*,*a*,*c*) axes of the crystal, the Poisson's ratios can be calculated using the C_{ij} values: ν_{zx} = -0.0111 and ν_{xz} = -0.0098, indicating small but negative Poisson's ratios for stretching along z (*c* axis) and along x (*b* axis), respectively; ν_{yx} = 0.2740 and ν_{xy} = 0.4393, ν_{yz} = 0.3095 and ν_{zy} = 0.5586, showing normal positive Poisson's ratios, albeit anisotropic. For bulk ZnTe, ν = 0.3533. Also found is that the hybrid has strongly enhanced shear response, about a factor of 5 as large, for the zx component compared to the bulk ZnTe. It means that a small shear stress along the *c* axis on the *b* plane can lead to a large distortion on the structure, which is understandable because along the *c* axis the inorganic slab is mot rigid and the molecules are aligned perpendicular to the *c* axis. These properties are yet to be confirmed experimentally and potentially can be used for high sensitivity stress sensing application.
2) **Stacked quasi 2D sheets** Quasi 2D materials, monolayer MoS_2 and alike, have many interesting properties. However, a single monolayer cannot offer adequate volume effect, for instance, optical absorption for certain applications (e.g., photo-detection). Attempting to stack them will result in drastic change in the material properties. It is thus highly desirable to be able to stack as many quasi 2D sheets as needed yet with minimal changes in the basic material properties. Hybrid structures, such as 3D hybrids $(ZnTe)_2C_nN_2H_{2n+4}$ (n = 0, 2- 5), could be the options for this purpose. The spacing between the inorganic slabs can be turned approximately from 4 to 10 Å to fine tune the electronic coupling between the inorganic slabs. This possibility offers unique opportunity to investigate the collective effects of electronically weakly coupled ultra-thin semiconductor layers, without the extreme sensitivity of the layer number dependence in systems like MoS_2.
3) **Room temperature exciton-polariton condensation** Large exciton binding energies (> 200 meV), sharp excitonic resonance (due to very high crystallinity), and excellent stability offer the II-VI hybrids unique advantages over other systems. The sharp resonance requires low energy input and the high ordering ensures long quantum coherence time. Exciton binding energy for β-ZnTe(en)$_{0.5}$ was estimated using effective mass theory [3], which is unlikely accurate for this type of system with the anticipated large exciton binding energy. A more rigorous theory, GW based approach solving Bethe-Salpeter equation, is required to offer

accurate understanding of the excitonic properties in these hybrids. Exciton-polariton effects can be explored in the similar manner as other less ordered hybrids [14].

4) **Phonon-polariton** β-ZnTe(en)$_{0.5}$ is perhaps the first semiconductor superlattice of which all Raman modes can be unambiguously identified [1], in contrast to all semiconductor superlattices known today (e.g., GaAs/AlAs) none of which has a Raman spectrum free of ambiguity in the assignments to at least some of its Raman modes due to inevitable structural fluctuations. The structural perfection of the II-VI hybrids allows the study of the phonon-polariton effects having a clean starting point. Many expected Raman modes of β-ZnTe(en)$_{0.5}$ have been identified by comparing with DFT calculated Raman mode frequencies and symmetries [1]. Polarized Raman spectra remain to be analyzed and compared with the calculated Raman tensors. Phonon polariton effects can then be explored.
5) **Carrier mobility** It has been shown that even along the inorganic/organic stacking direction, β-ZnTe(en)$_{0.5}$ exhibits a mobility close to 10^{-2} cm^2/(V s) at room temperature [1], which is much better than the bulk mobilities in all semiconducting organic materials. It can be further enhanced by changing the spacer molecule. The in-plane mobility has been measured to be around 100 cm^2/(Vs) (Zhang group, unpublished), which is as good as inorganic semiconductors like GaN and CdTe. These results ensure the feasibility of practical applications of these materials.
6) **UV device applications** UV light emitting and detecting devices can benefit from the ultra-strong band edge absorption and oscillator strength. The transparency to the full visible spectrum can be utilized for fabricating transparent electronic devices (e.g., transistors and sensors).
7) **Thermoelectric application** β-ZnTe(en)$_{0.5}$ has been predicted, although not yet measured, to have roughly a factor of 10 reduction in thermal conductivities [13]. Coupling with the measured high carrier mobility (much better than most thermoelectric materials), the 3D II-VI hybrids are of great interest for exploring thermoelectric applications.
8) **Epitaxial growth of the hybrid materials** Most practical device applications adopt a thin-film like device geometry. The ability to form the hybrid thin films on different substrates are important for a wide range of applications. Very recently we have achieved preliminary success in forming some hybrid structures on foreign substrates (unpublished).

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