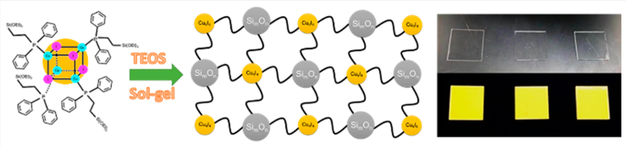
Inorganic Chemistry

Incorporation of an Emissive Cu_4I_4 Core into Cross-Linked Networks: An Effective Strategy for Luminescent Organic–Inorganic Hybrid Coatings

Hua Tong, Haibo Li, Haojun Li, Cidanpuchi, Fuchen Wang, and Wei Liu*

Cite This: https://doi.org/10.1021/acs.inorgchem.1c00909 Read Online

ABSTRACT: Here, an effective strategy for the preparation of luminescent organic–inorganic hybrid coatings (OIHCs) by the incorporation of an emissive Cu_4I_4 core into cross-linked coating networks through coordination bonds is reported. The luminescent coatings obtained show potential application in a variety of areas, and such a synthetic strategy of the incorporation of an emissive inorganic core into extended networks has proven to be an efficient method for the synthesis of luminescent OIHCs.



Organic–inorganic hybrid materials have been known for decades, and these hybrid compounds exhibit unique properties.[1−4] The combination of inorganic species and organic ligands leverages the advantages of both components and would lead to new and novel properties.[5,6] Scientists can easily alter the structure of hybrid compounds to investigate their structure–property relationships.[7−10] These hybrid structures exhibit potential applications in a variety of areas, including solid-state lighting, solar cells, functional coatings, etc.[9,11−17] Better-performance functional hybrid structures are in high demand in these areas.

Corrosion has always been a worldwide problem because it attacks our environment and may have serious consequences.[18−21] Protective coatings are the most direct and effective way to protect metallic materials from corrosion.[22−25] Organic–inorganic hybrid coatings (OIHCs) are a very important application of organic–inorganic hybrid materials. The OIHCs display various advantages compared to pure organic or inorganic coatings, such as low volatile organic content, good corrosion protection and adhesion properties on metallic substrates, etc. One of the commonly used methods to synthesize OIHCs is the sol–gel method, and tetraethoxysilane (TEOS) is typically used as the precursor that undergoes hydrolysis and condensation reactions, forming a self-assembled network.[26−29] The formed coatings prevent contact between the corrosive species and metallic substrates, and their protective properties can be systematically tuned by adjusting the reaction conditions and the composition of the coating materials.[30−32]

In order to achieve better performance and more functionalities, the development of multifunctional coatings with luminescence, self-healing ability, high-thermal stability, and mechanical resistance have been very hot topics.[21,33−36] Among them, luminescent coatings represent an important class of functional coatings, and they can be used as intelligent coatings, which are able to respond to changes in the environment for the applications in monitoring and early warning of corrosion.[37−39] They can also be used as decorative coatings, anticounterfeiting printings, art paintings, etc.[40] At present, the luminescent OIHCs are mainly prepared by adding luminescent materials, such as phosphors, into the hybrid coatings to achieve the light-emitting performance.[41,42] Such a physical mixing of the multicomponents may lead to the problem of nonuniform dispersion of the luminophores and the precipitation of luminescent particles. In addition, the phosphors used are generally rare-earth-based and may bring environmental issues. Therefore, developing new and facile strategies for better-performing luminescent OIHCs is of great significance.

Inspired by the early studies, we report an effective strategy for the preparation of luminescent OIHCs by the incorporation of an emissive Cu_4I_4 core into cross-linked coating networks through coordination bonds.[43−48] Phosphines are common organic ligands for the synthesis of copper iodide based hybrid structures. One of the most used members, triphenylphosphine (tpp) has been frequently used for the construction of Cu_2I_2 or Cu_4I_4 discrete cluster-based compounds because of the steric hindrance of the tpp molecules.[49] Here, a tpp derivative, P-containing silane coupling agent 2-(diphenylphosphino)ethyltriethoxysilane (dpes) with a structure similar to that of tpp, has been selected as the precursor for the preparation of OIHCs (Figure S1). The P atoms on dpes would coordinate to Cu, forming a

Received: March 29, 2021

Cu_4I_4 core when reacted with CuI, resulting in a new Cu_4I_4-cluster-containing silane coupling agent (Cu_4I_4-dpes; Figure 1a). Cu_4I_4-dpes could be further hydrolyzed and condensed with other coupling reagents to form cross-linked OIHCs (Figure 1c). The proposed strategy is suitable for the large-scale preparation of strongly luminescent and stable Cu_4I_4-based hybrid coating materials. dpes not only plays an important role in the formation of a Cu_4I_4 core but also as a coupling reagent, forming cross-linked coating networks.

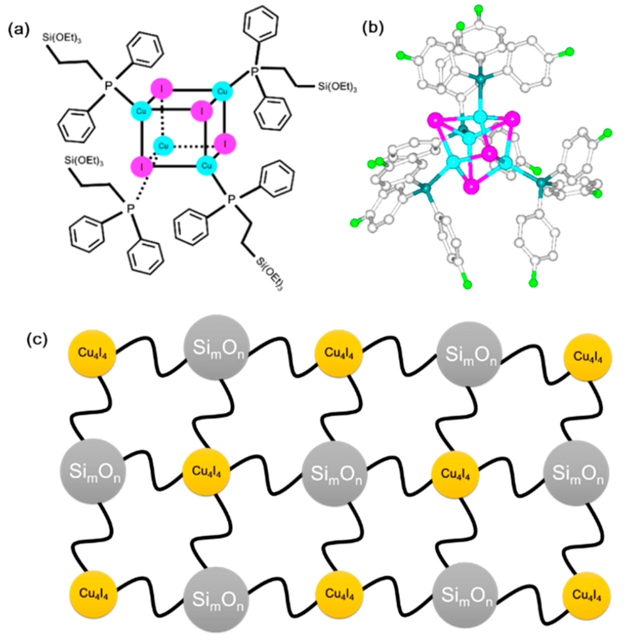


Figure 1. (a) Structural plot of synthesized Cu_4I_4-dpes. (b) Structure plot of 0D-Cu_4I_4(F-tpp)$_4$. (c) Illustration of the cross-linked network structure of compound **1**.

The Cu_4I_4 emissive inorganic core has been well-studied for its phosphorescence originating from the strong Cu−Cu interaction.[44,50−52] Cu_4I_4 cubane tetramer-based structures have the general formula $Cu_4I_4(L)_n$ and have been intensively studied.[44,45] The shorter Cu−Cu distance (less than the sum of the van der Waals radii 2.8 Å) in the Cu_4I_4 core leads to a series of unique optical properties. Thermochromic and mechanochromic luminescence has been reported for Cu_4I_4-based clusters.[53,54] Cu_4I_4-based extended structures are typically more stable compared to molecular clusters of this type.[44,46]

The preparation of Cu_4I_4-dpes was conducted in reaction vials at room temperature. dpes was added into a suspension CuI in dichloromethane. The reaction mixture was stirred for a few hours at room temperature and filtered. Interestingly, the reaction mixture became almost transparent after the reaction, indicating that the insoluble CuI in the reaction mixture has reacted with dpes. A high-viscosity transparent oil Cu_4I_4-dpes was obtained after the slow evaporation of dichloromethane, emitting a strong yellow emission under UV-light irradiation. Because all of the reactants are not luminescent, the yellow emission from the oil indicates the formation of an emissive Cu_4I_4 core in the extended structures. Because single crystals of this compound could not be obtained, we used another phosphine ligand, tris(4-fluorophenyl)phosphane (F-tpp), as the organic ligand instead of dpes for the reaction with CuI and obtained single crystals (Figure S2). The single-crystal X-ray diffraction results show that it is a Cu_4I_4 cubane tetramer-based molecular cluster, 0D-Cu_4I_4(F-tpp)$_4$ (Figure 1b). The detailed crystallographic data have been summarized in Table S1. The power X-ray diffraction (PXRD) patterns of 0D-Cu_4I_4(F-tpp)$_4$ are shown in Figure S3. The resemblance of the structures of the organic ligands and the reaction conditions indicate that it is highly possible that the transparent oil formed is a Cu_4I_4-based structure. The ^{1}H NMR spectrum of Cu_4I_4-dpes is shown in Figure S4. OIHCs were further prepared by a sol−gel method with Cu_4I_4-dpes and TEOS under acidic conditions. The transparent viscous liquid was obtained by evaporation of the solvent. The liquid was uniformly coated onto quartz substrates by a spin-coating technique. A uniform coating film was formed on a quartz substrate with a thickness of 3 μm (Figure S5). The OIHC materials have been completely dried as a white powder (compound **1**) for structural and optical characterizations.

X-ray photoelectron spectroscopy (XPS) was employed to confirm the composition of the OIHC material. As shown in

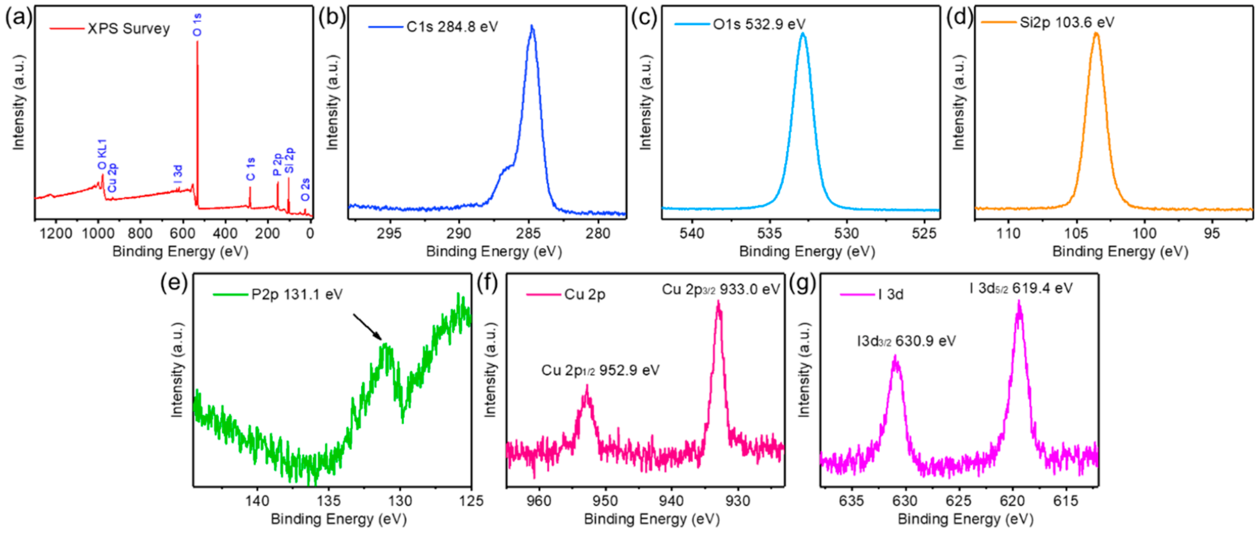


Figure 2. (a) XPS spectra of the (a) survey, (b) C 1s, (c) O 1s, (d) Si 2p, (e) P 2p, (f) Cu 2p, and (g) I 3d of the OIHC material.

Figure 2a, only the C, O, Si, P, Cu, and I elements are detected in the XPS survey, indicating the high purity of the OIHC coating. In the C 1s XPS spectrum (Figure 2b), the main peak at 284.8 eV is consistent with the dominant phenyl contribution.[43] The minor peak at around 286 eV should have originated from the adventitious atmospheric organic pollutants. The O 1s and Si 2p spectra (Figure 2c,d) possess highly symmetric peaks at 532.9 and 103.6 eV, respectively, indicating a uniform Si−O−Si major constitution and coinciding with the SiO_2 sol−gel configuration with silicon-(IV) species.[43] The P 2p signal at 131.1 eV is in agreement with the reported P atom corresponding to the phosphine ligand coordinated to Cu atoms (Figure 2e).[55] As for the Cu and I elements, both Cu $2p_{3/2}$ at 933.0 eV and I $3d_{5/2}$ at 619.4 eV are consistent with the Cu_4I_4 XPS data from the literature (933.00 and 619.72 eV, respectively), demonstrating the existence of Cu_4I_4 (Figure 2f,g).[43] Notably, the atomic percentages of P, Cu, and I are 0.3%, 0.25%, and 0.2%, respectively (Table S2), indicating that the P/Cu/I ratio is approximatively 1/1/1.

In the OIHC material obtained, there are two types of inorganic species: CuI and silica. The two types of inorganic cores are interconnected by the organic species, forming a cross-linked network (Figure 1c). PXRD analyses have been carried out, and the results show that the as-made network is totally amorphous structure (Figure 3a). No peak for CuI has been observed in the PXRD pattern, indicating full incorporation of the inorganic component in the network structure. Fourier transform infrared (FT-IR) spectroscopy shows that the sample exhibited a strong absorption peak at 792 cm^{-1}, corresponding to the absorption peaks of the Si−O−Si stretching and Si−O−Si bending vibrations, respectively (Figure 3b). The absorption peaks of the stretching vibrations of $-CH_3$ and $-CH_2-$ in the range of 3000−2800 cm^{-1} as well as the C═C stretching vibration of a double bond at 1640 cm^{-1} demonstrate the successful reaction of Cu_4I_4-dpes with TEOS via a sol−gel method.

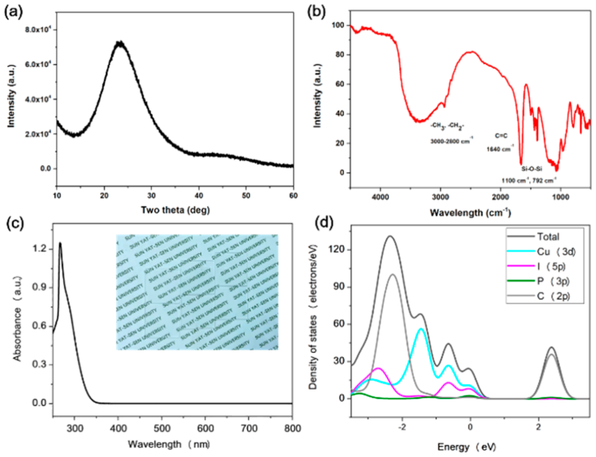


Figure 3. (a) PXRD patterns of compound **1**. (b) FT-IR spectrum of compound **1**. (c) UV−vis absorption spectrum of coatings on quartz. Inset: Photograph of the quartz coated with the hybrid material. (d) DOS plot of 0D-Cu_4I_4(F-tpp)$_4$.

Optical diffuse-reflectance spectra were collected at room temperature. The dried sample of the OIHC material is colorless, and the absorption spectrum shows that the OIHC material exhibits no absorption in the visible-light region. The coatings on the quartz substrates are transparent (inset of Figure 3b). Because the Cu_4I_4 core is incorporated in the hybrid coatings, the optical properties of **1** are similar compared to that of other Cu_4I_4-based hybrid structures. Density of states (DOS) calculations of 0D-Cu_4I_4(F-tpp)$_4$ (Figure 3d) demonstrate similarities and differences in the atomic state distributions compared to other Cu_4I_4-based hybrid structures, indicating that the optical properties of the Cu_4I_4-based hybrid coatings can be systematically tuned by changing either the inorganic species or organic ligands.[44,45,45]

The photoluminescence (PL) spectrum of compound **1** is shown in Figure 4a. The yellow emission peak at 580 nm has a full width at half-maximum (fwhm) of around 110 nm. A 40 nm blue shift was observed compared to its precursor Cu_4I_4-dpes (Figure S6). Compound **1** shows a large Stokes shift of ∼325 nm, exhibiting a large energy-level difference between the absorption excitation state and PL emission state. Compared to the emission of 0D-Cu_4I_4(F-tpp)$_4$, compound **1** shows a red shift of around 30 nm (Figure S7). The internal quantum yield of **1** was measured to be 8.5% under 300 nm excitation, which is relatively lower compared to those of other Cu_4I_4-based compounds.[44] The Commission Internationale de l'Eclairage (CIE) chromaticity coordinates (Figure 4b) for the emission were calculated to be (0.49, 0.50), indicating that the emission of compound **1** is orange-yellow light.

As shown in previous studies for Cu_4I_4-based clusters, thermochromic luminescence of compound **1** is revealed by immersion of **1** in liquid nitrogen.[54] Under the same UV excitation, the orange-yellow emission becomes a sharp-yellow emission (inset of Figure S8). The emission spectrum of compound **1** at 77 K has been collected (Figure S8), which shows that the emission intensity increases and the emission band becomes narrower at lowered temperatures. Also, blue shifts in the emission energies have been observed as the temperature is decreased. About a 20 nm blue shift in its emission spectrum was observed by lowering the temperature from room temperature to 77 K. This can be explained by the reduced structural torsion and increased localization of the excited state on the $Cu_4I_4L_4$ cluster.[56] Figure S9 displays the luminescence decay of **1** at room temperature, and it shows that compound **1** has a long lifetime of approximately 2.35 μs by monoexponential fitting. This is in accordance with the lifetime values of other luminescent Cu_4I_4-based organic−inorganic hybrid materials.[45]

The sol−gel coating materials are luminescent under UV excitation (inset of Figure 4a) and can be coated onto the various kinds of substrates by a spin-coating technique. The detailed coating preparation procedure is described in the Supporting Information. After coating with **1**, it can be seen that the quartz substrates are completely transparent under nature light. Upon 254 nm UV-light irradiation, the quartzes exhibit intense yellow-light signals (Figure 4c). The scanning electron microscopy (SEM) image shows the formation of a uniform, homogeneous, crack-free, and highly adherent protective film on the rectangular quartz substrate coated with hybrid coatings (Figure S5). The coatings can also be coated on metallic surfaces, as shown in the inset of Figure 4b. The luminescent coatings show good air and moisture stability. After the coated quartz was exposed to open air for 1 month, no noticeable change in the luminescent intensity is observed. After the coated quartz was heated at 45 °C overnight, the surface morphology and luminescence intensity of the coatings show negligible changes (Figure S10). However, the coatings

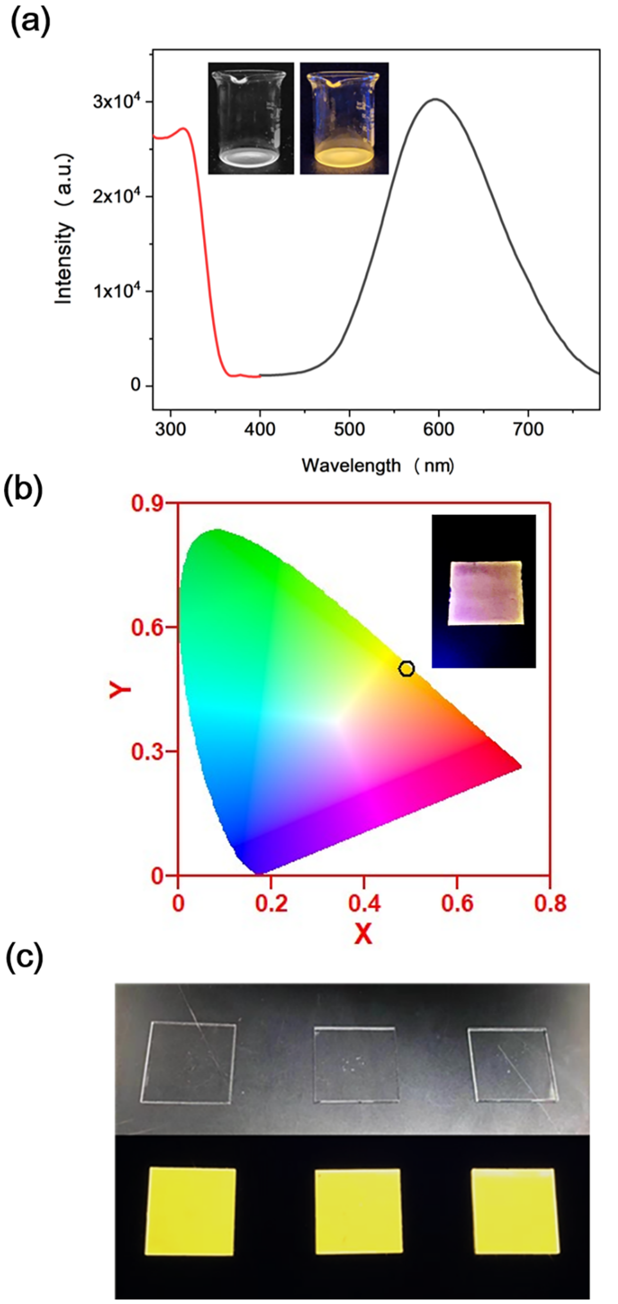


Figure 4. (a) Excitation (red) and emission (black) spectra of coatings on quartz. λ_{em} = 580 nm; λ_{ex} = 300 nm. Inset: Sol−gel coating solution under nature and UV light. (b) CIE coordinates of compound **1**. Inset: Coated carbon steel Q235 under 254 nm UV light. (c) Images of the coated quartz under natural light (top) and 254 nm UV light (bottom).

show an obvious luminescence decrease upon heating at elevated temperatures.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00909.

Structural plot of the organic ligands, PL spectra, SEM images, and crystallographic data (PDF)

Accession Codes

CCDC 1999514 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Wei Liu − *School of Chemical Engineering and Technology, Sun Yat-Sen University, Zhuhai 519082, China;* orcid.org/0000-0002-8543-1605; Email: liuwei96@mail.sysu.edu.cn

Authors

Hua Tong − *School of Chemical Engineering and Technology, Sun Yat-Sen University, Zhuhai 519082, China*
Haibo Li − *School of Chemical Engineering and Technology, Sun Yat-Sen University, Zhuhai 519082, China*
Haojun Li − *School of Chemical Engineering and Technology, Sun Yat-Sen University, Zhuhai 519082, China*
Cidanpuchi − *School of Chemical Engineering and Technology, Sun Yat-Sen University, Zhuhai 519082, China*
Fuchen Wang − *School of Chemical Engineering and Technology, Sun Yat-Sen University, Zhuhai 519082, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.1c00909

Author Contributions

H.T. and H.L. carried out the experiment. H.L., C., and F.W. contributed to the sample preparation and characterizations. W.L. wrote the manuscript. All authors discussed the results and contributed to the final manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The National Natural Science Foundation of China (Grants 21901167 and U20A20233), the Shenzhen Science and Technology Research grant (Grant JCYJ20180307102051326), the Start-up Fund of Sun Yat-Sen University (76110-18841231), and the Science and Technology Program of Guangzhou (202102021177) are greatly acknowledged.

■ REFERENCES

(1) Huang, X.; Li, J. From Single to Multiple Atomic Layers: A Unique Approach to the Systematic Tuning of Structures and Properties of Inorganic−Organic Hybrid Nanostructured Semiconductors. *J. Am. Chem. Soc.* **2007**, *129*, 3157−3162.

(2) Huang, X. Y.; Li, J.; Zhang, Y.; Mascarenhas, A. From 1D chain to 3D network: Tuning hybrid II-VI nanostructures and their optical properties. *J. Am. Chem. Soc.* **2003**, *125*, 7049−7055.

(3) Kagan, C. R.; Mitzi, D. B.; Dimitrakopoulos, C. D. Organic-Inorganic Hybrid Materials as Semiconducting Channels in Thin-Film Field-Effect Transistors. *Science* **1999**, *286*, 945−947.

(4) Mitzi, D. B. Synthesis, Structure, and Properties of Organic-Inorganic Perovskites and Related Materials. *Progress in Inorganic Chemistry*; John Wiley & Sons, Inc., 2007; pp 1−121.

(5) Saparov, B.; Mitzi, D. B. Organic−Inorganic Perovskites: Structural Versatility for Functional Materials Design. *Chem. Rev.* **2016**, *116*, 4558−4596.

(6) Li, J.; Zhang, R. A New Class of Nanostructured Inorganic−Organic Hybrid Semiconductors Based on II−VI Binary Compounds. *Progress in Inorganic Chemistry*; John Wiley & Sons, Inc., 2011; pp 445−504.

(7) Mao, L.; Guo, P.; Kepenekian, M.; Hadar, I.; Katan, C.; Even, J.; Schaller, R. D.; Stoumpos, C. C.; Kanatzidis, M. G. Structural Diversity in White-Light-Emitting Hybrid Lead Bromide Perovskites. *J. Am. Chem. Soc.* **2018**, *140*, 13078−13088.

(8) Fang, X.; Roushan, M.; Zhang, R.; Peng, J.; Zeng, H.; Li, J. Tuning and Enhancing White Light Emission of II−VI Based Inorganic−Organic Hybrid Semiconductors as Single-Phased Phosphors. *Chem. Mater.* **2012**, *24*, 1710−1717.

(9) Cao, Y.; Wang, N.; Tian, H.; Guo, J.; Wei, Y.; Chen, H.; Miao, Y.; Zou, W.; Pan, K.; He, Y.; Cao, H.; Ke, Y.; Xu, M.; Wang, Y.; Yang, M.; Du, K.; Fu, Z.; Kong, D.; Dai, D.; Jin, Y.; Li, G.; Li, H.; Peng, Q.; Wang, J.; Huang, W. Perovskite light-emitting diodes based on spontaneously formed submicrometre-scale structures. *Nature* **2018**, *562*, 249−253.

(10) Wang, J.; Wang, N.; Jin, Y.; Si, J.; Tan, Z.-K.; Du, H.; Cheng, L.; Dai, X.; Bai, S.; He, H.; Ye, Z.; Lai, M. L.; Friend, R. H.; Huang, W. Interfacial Control Toward Efficient and Low-Voltage Perovskite Light-Emitting Diodes. *Adv. Mater.* **2015**, *27*, 2311−2316.

(11) Liu, F.; Liu, A.; Tao, W.; Yang, Y. Preparation of UV curable organic/inorganic hybrid coatings-a review. *Prog. Org. Coat.* **2020**, *145*, 105685.

(12) Zvonkina, I. J.; Soucek, M. D. Inorganic−organic hybrid coatings: common and new approaches. *Curr. Opin. Chem. Eng.* **2016**, *11*, 123−127.

(13) Ki, W.; Li, J. A Semiconductor Bulk Material That Emits Direct White Light. *J. Am. Chem. Soc.* **2008**, *130*, 8114−8115.

(14) Ki, W.; Li, J.; Eda, G.; Chhowalla, M. Direct white light emission from inorganic−organic hybrid semiconductor bulk materials. *J. Mater. Chem.* **2010**, *20*, 10676−10679.

(15) Dohner, E. R.; Jaffe, A.; Bradshaw, L. R.; Karunadasa, H. I. Intrinsic White-Light Emission from Layered Hybrid Perovskites. *J. Am. Chem. Soc.* **2014**, *136*, 13154−13157.

(16) Green, M. A.; Ho-Baillie, A.; Snaith, H. J. The emergence of perovskite solar cells. *Nat. Photonics* **2014**, *8*, 506.

(17) Guner, T.; Demir, M. M. A Review on Halide Perovskites as Color Conversion Layers in White Light Emitting Diode Applications. *Phys. Status Solidi A* **2018**, *215*, 1800120.

(18) Figueira, R. B.; Sousa, R.; Silva, C. J. R. Multifunctional and smart organic−inorganic hybrid sol−gel coatings for corrosion protection applications. In *Advances in Smart Coatings and Thin Films for Future Industrial and Biomedical Engineering Applications*; Makhlouf, A. S. H., Abu-Thabit, N. Y., Eds.; Elsevier, 2020; Chapter 3, pp 57−97.

(19) Birbilis, N.; Hinton, B. Corrosion and corrosion protection of aluminium. In *Fundamentals of Aluminium Metallurgy*; Lumley, R., Ed.; Woodhead Publishing, 2011; Chapter 19, pp 574−604.

(20) Cohen, S. M. Review: Replacements for Chromium Pretreatments on Aluminum. *Corrosion* **1995**, *51*, 71−78.

(21) Lee, C. K. Corrosion and wear-corrosion resistance properties of electroless Ni−P coatings on GFRP composite in wind turbine blades. *Surf. Coat. Technol.* **2008**, *202*, 4868−4874.

(22) Montemor, M. F. Functional and smart coatings for corrosion protection: A review of recent advances. *Surf. Coat. Technol.* **2014**, *258*, 17−37.

(23) Ballard, R. L.; Williams, J. P.; Njus, J. M.; Kiland, B. R.; Soucek, M. D. Inorganic−organic hybrid coatings with mixed metal oxides. *Eur. Polym. J.* **2001**, *37*, 381−398.

(24) Ding, R.; Chen, S.; Lv, J.; Zhang, W.; Zhao, X.-d.; Liu, J.; Wang, X.; Gui, T.-j.; Li, B.-j.; Tang, Y.-z.; Li, W.-h. Study on graphene modified organic anti-corrosion coatings: A comprehensive review. *J. Alloys Compd.* **2019**, *806*, 611−635.

(25) Ding, R.; Li, W.; Wang, X.; Gui, T.; Li, B.; Han, P.; Tian, H.; Liu, A.; Wang, X.; Liu, X.; Gao, X.; Wang, W.; Song, L. A brief review of corrosion protective films and coatings based on graphene and graphene oxide. *J. Alloys Compd.* **2018**, *764*, 1039−1055.

(26) Balaji, J.; Roh, S.-H.; Edison, T. N. J. I.; Jung, H.-Y.; Sethuraman, M. G. Sol-gel based hybrid silane coatings for enhanced corrosion protection of copper in aqueous sodium chloride. *J. Mol. Liq.* **2020**, *302*, 112551.

(27) Adhami, S.; Atapour, M.; Allafchian, A. R. Corrosion protection of copper by silane sol−gel coatings. *J. Sol-Gel Sci. Technol.* **2015**, *74*, 800−809.

(28) Pehkonen, S. O.; Yuan, S.: Inorganic−Organic Hybrid Coatings. In *Interface Science and Technology*; Pehkonen, S. O., Yuan, S., Eds.; Elsevier, 2018; Vol. *23*, Part 5, pp 115−132.

(29) Ye, Y.; Liu, W.; Liu, Z.; Zhang, D.; Zhao, H.; Wang, L.; Li, X. Anti-corrosion performance of aniline trimer-containing sol−gel hybrid coatings for mild steel substrate. *J. Sol-Gel Sci. Technol.* **2018**, *87*, 464−477.

(30) Guo, F.; Gao, J.; Li, X. RESEARCH PROGRESS ON TITANIUM-CONTAINING ORGANIC−INORGANIC HYBRID PROTECTIVE COATINGS. *Surf. Rev. Lett.* **2019**, *26*, 1930002.

(31) Wen, J.; Wilkes, G. L. Organic/Inorganic Hybrid Network Materials by the Sol−Gel Approach. *Chem. Mater.* **1996**, *8*, 1667−1681.

(32) Yamabe, H. Stabilization of the polymer-metal interface. *Prog. Org. Coat.* **1996**, *28*, 9−15.

(33) Jian, X.; Hu, Y.; Zhou, W.; Xiao, L. Self-healing polyurethane based on disulfide bond and hydrogen bond. *Polym. Adv. Technol.* **2018**, *29*, 463−469.

(34) Li, T.; Xie, Z.; Xu, J.; Weng, Y.; Guo, B.-H. Design of a self-healing cross-linked polyurea with dynamic cross-links based on disulfide bonds and hydrogen bonding. *Eur. Polym. J.* **2018**, *107*, 249−257.

(35) Xu, C.; Zhan, W.; Tang, X.; Mo, F.; Fu, L.; Lin, B. Self-healing chitosan/vanillin hydrogels based on Schiff-base bond/hydrogen bond hybrid linkages. *Polym. Test.* **2018**, *66*, 155−163.

(36) Pourhashem, S.; Saba, F.; Duan, J.; Rashidi, A.; Guan, F.; Nezhad, E. G.; Hou, B. Polymer/Inorganic nanocomposite coatings with superior corrosion protection performance: A review. *J. Ind. Eng. Chem.* **2020**, *88*, 29−57.

(37) Sano, K.; Kanematsu, H.; Tanaka, T. Overview of Silane-Based Polymer Coatings and Their Applications. In *Industrial Applications for Intelligent Polymers and Coatings*; Hosseini, M., Makhlouf, A. S. H., Eds.; Springer International Publishing: Cham, Switzerland, 2016; pp 493−509.

(38) Latif, J.; Khan, Z. A.; Stokes, K. Structural monitoring system for proactive detection of corrosion and coating failure. *Sens. Actuators, A* **2020**, *301*, 111693.

(39) Miyazawa, M. Advanced corrosion control at chemical plants using a new corrosion monitoring technique. In *Techniques for Corrosion Monitoring*; Yang, L., Ed.; Woodhead Publishing, 2008; Part 25, pp 601−613.

(40) Wang, J.-J.; Chen, C.; Chen, W.-G.; Yao, J.-S.; Yang, J.-N.; Wang, K.-H.; Yin, Y.-C.; Yao, M.-M.; Feng, L.-Z.; Ma, C.; Fan, F.-J.; Yao, H.-B. Highly Luminescent Copper Iodide Cluster Based Inks with Photoluminescence Quantum Efficiency Exceeding 98%. *J. Am. Chem. Soc.* **2020**, *142*, 3686−3690.

(41) Younis, O.; El-Katori, E. E.; Hassanien, R.; Abousalem, A. S.; Tsutsumi, O. Luminescent coatings: White-color luminescence from a simple and single chromophore with high anticorrosion efficiency. *Dyes Pigm.* **2020**, *175*, 108146.

(42) Dantelle, G.; Salaün, M.; Bruyère, R.; Kodjikian, S.; Ibanez, A. Luminescent coatings prepared from optimized YAG:Ce nanoparticles. *Thin Solid Films* **2017**, *643*, 36−42.

(43) Tard, C.; Perruchas, S.; Maron, S.; Le Goff, X. F.; Guillen, F.; Garcia, A.; Vigneron, J.; Etcheberry, A.; Gacoin, T.; Boilot, J.-P. Thermochromic Luminescence of Sol−Gel Films Based on Copper Iodide Clusters. *Chem. Mater.* **2008**, *20*, 7010−7016.

(44) Fang, Y.; Liu, W.; Teat, S. J.; Dey, G.; Shen, Z.; An, L.; Yu, D.; Wang, L.; O'Carroll, D. M.; Li, J. A Systematic Approach to Achieving High Performance Hybrid Lighting Phosphors with Excellent Thermal- and Photostability. *Adv. Funct. Mater.* **2017**, *27*, 1603444.

(45) Liu, W.; Fang, Y.; Li, J. Copper Iodide Based Hybrid Phosphors for Energy-Efficient General Lighting Technologies. *Adv. Funct. Mater.* **2018**, *28*, 1705593.

(46) Liu, W.; Lustig, W. P.; Li, J. Luminescent inorganic-organic hybrid semiconductor materials for energy-saving lighting applications. *EnergyChem.* **2019**, *1*, 100008.

(47) Liu, W.; Fang, Y.; Wei, G. Z.; Teat, S. J.; Xiong, K.; Hu, Z.; Lustig, W. P.; Li, J. A Family of Highly Efficient CuI-Based Lighting Phosphors Prepared by a Systematic, Bottom-up Synthetic Approach. *J. Am. Chem. Soc.* **2015**, *137*, 9400−9408.

(48) Hei, X.; Liu, W.; Zhu, K.; Teat, S. J.; Jensen, S.; Li, M.; O'Carroll, D. M.; Wei, K.; Tan, K.; Cotlet, M.; Thonhauser, T.; Li, J. Blending Ionic and Coordinate Bonds in Hybrid Semiconductor Materials: A General Approach toward Robust and Solution-Processable Covalent/Coordinate Network Structures. *J. Am. Chem. Soc.* **2020**, *142*, 4242−4253.

(49) Liu, W.; Zhu, K.; Teat, S. J.; Deibert, B. J.; Yuan, W.; Li, J. A mechanochemical route toward the rational, systematic, and cost-effective green synthesis of strongly luminescent copper iodide based hybrid phosphors. *J. Mater. Chem. C* **2017**, *5*, 5962−5969.

(50) Kyle, K. R.; Ryu, C. K.; Ford, P. C.; DiBenedetto, J. A. Photophysical studies in solution of the tetranuclear copper(I) clusters Cu4I4L4 (L = pyridine or substituted pyridine). *J. Am. Chem. Soc.* **1991**, *113*, 2954−2965.

(51) Rath, N. P.; Holt, E. M.; tanimura, K. Fluorescent copper(I) complexes: correlation of structural and emission characteristics of [{CuI(quin)2}2] and [Cu4I4(quin)4](quin = quinoline). *J. Chem. Soc., Dalton Trans.* **1986**, 2303−2310.

(52) Ford, P. C.; Cariati, E.; Bourassa, J. Photoluminescence Properties of Multinuclear Copper(I) Compounds. *Chem. Rev.* **1999**, *99*, 3625−3648.

(53) Li, S.-L.; Zhang, F.-Q.; Zhang, X.-M. An organic-ligand-free thermochromic luminescent cuprous iodide trinuclear cluster: evidence for cluster centered emission and configuration distortion with temperature. *Chem. Commun.* **2015**, *51*, 8062−8065.

(54) Perruchas, S.; Le Goff, X. F.; Maron, S.; Maurin, I.; Guillen, F.; Garcia, A.; Gacoin, T.; Boilot, J.-P. Mechanochromic and Thermochromic Luminescence of a Copper Iodide Cluster. *J. Am. Chem. Soc.* **2010**, *132*, 10967−10969.

(55) Battistoni, C.; Mattogno, G.; Paparazzo, E.; Naldini, L. An XPS and Auger study of some polynuclear copper compounds. *Inorg. Chim. Acta* **1985**, *102*, 1−3.

(56) Liu, W.; Zhu, K.; Teat, S. J.; Dey, G.; Shen, Z.; Wang, L.; O'Carroll, D. M.; Li, J. All-in-One: Achieving Robust, Strongly Luminescent and Highly Dispersible Hybrid Materials by Combining Ionic and Coordinate Bonds in Molecular Crystals. *J. Am. Chem. Soc.* **2017**, *139*, 9281−9290.

https://doi.org/10.1021/acs.inorgchem.1c00909