

Single-Component MLCT-Active Photodetecting Material Based on a Two-Dimensional Coordination Polymer

Qing-Qing Huang^{1,2†}, Yan-Zhou Li^{1,2†}, Zhi Zheng³, Xiao-Ming Jiang^{1,2}, Shan-Shan Sun⁴, Hui-Jie Jiang^{1,2}, Wei-Hua Deng^{1,2}, Guan-E Wang^{1,2}, Tian-You Zhai^{3*}, Ming-De Li^{4*} & Gang Xu^{1,2*}

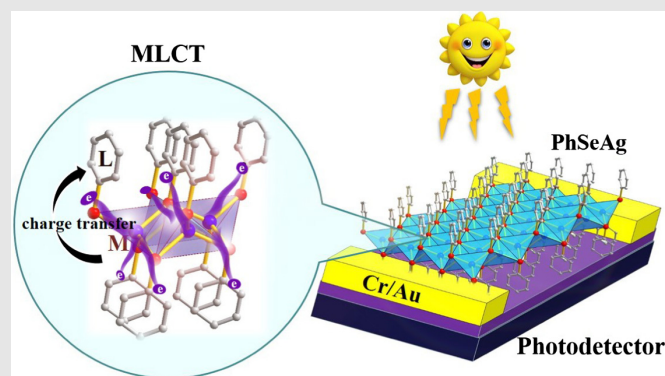
¹State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences (CAS), Fuzhou, Fujian 350002 (China), ²University of Chinese Academy of Sciences (UCAS), Beijing 100049, (China), ³State Key Laboratory of Material Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology (HUST), Wuhan 430074, (China), ⁴Department of Chemistry and Key Laboratory for Preparation and Application of Ordered Structural Materials of Guangdong Province, Shantou University, Shantou 515063, (China)

*Corresponding authors: gxu@fjirsm.ac.cn; zhaity@hust.edu.cn; mdli@stu.edu.cn; †Q.-Q. Huang and Y.-Z. Li contributed equally to this work

Cite this: *CCS Chem.* **2019**, *1*, 655–662

Conductive coordination polymers (CCPs) have shown great potential for electronic purposes. However, their applications in photodetection have been limited by poor sensitivity, low on/off current ratio, and slow response owing to the low charge generation and/or separation efficiency. In this work, metal-to-ligand charge-transfer (MLCT) in PhSeAg was used to fabricate a single-component MLCT photodetecting material for the first time to solve the above challenges. The material obtained possesses ultrahigh sensitivity to weak-light intensity (0.03 mW cm^{-2}), the highest on/off ratio, and the fastest response speed than other well-known CCPs materials tested. Our work might provide a simple but common strategy for

designing high-performance CCPs composites for optoelectrical applications.



Keywords: coordination polymer, metal-organic chalcogenide, metal-to-ligand charge transfer, semiconductor, optoelectronic material

Introduction

Coordination polymers are a class of crystalline materials that are constructed by the coordination of inorganic secondary building units (metal ions or clusters) and

organic linkers.^{1–3} Recently, one of their sub-branches, termed conductive coordination polymers (CCPs), have attracted growing interest. The abundance and designable building blocks of CCPs provide them with endless possibilities of tuning their electrical properties to enable

their promising applications as field-effect transistors, thermoelectric devices, chemiresistive gas sensors, electrochromic devices, and others.^{4,5} However, the application of CCPs in photodetection is still limited by the low generation and separation efficiency of the photoexcited charge carriers. Thus, it is highly desirable to explore an effective structural design method to enhance the photo-detecting performances of CCPs. The existing efforts for improving the performances of photodetecting materials include constructing heterojunctions, compositing with other materials, or doping with other elements/quantum dots.^{6–8} Among them, dispersing discrete metal–organic complexes, that readily undergo metal-to-ligand charge-transfer (MLCT), and processing them into composite and efficient conductive materials is very attractive,^{9,10} because MLCT could promote the generation and separation of photoexcited charge carrier.^{11–13} For example, when graphene, a monolayer of crystalline carbon, was composited with an MLCT ruthenium(II) tris(bipyridyl) compound, the fabrication showed enhanced response to visible light by two orders of magnitude. However, this type of composite material required relative tedious preparation procedures, such as individually preparing the MLCT component, the conductive component, and subsequently, combining both of them (Figure 1). To simplify the preparation procedure, we envisaged that directly integrating the MLCT component into CCP might be a feasible strategy. Moreover, this approach would allow merging both the merits of MLCT component and CCP into one material to obtain a high-performance photodetection material.

Through literature searches, we found that the reported coordination polymer of silver nanocluster,

PhSeAg (PhSeH = selenophenol), represents a good model for the demonstration of our material design strategy, although its optoelectrical properties have not been reported yet.¹⁴ In **PhSeAg**, Ag⁺ is in a low oxidation state, and hence, could facilitate the donation of excited electrons to ligands, whereas PhSeH with the low-lying π^* orbital, is favorable for the acceptance of electrons transferred from the metal centers. Therefore, under light irradiation, the induction of MLCT within **PhSeAg** is expected. Moreover, apart from **PhSeAg** being different from the common coordination polymers, it possesses a two-dimensional (2D) inorganic continuous {AgSe}_n layer, likely to enable smooth charge transport through the whole material. The results of the optoelectrical measurements using semiconductor characterization system (4200SCS, Keithley, USA), revealed that the Conductive Coordination Polymer (CCP)-**PhSeAg** showed not only strong response over whole visible-light range, but also, demonstrated ultrahigh sensitivity to weak light, the highest on/off ratio, and an overall fastest turn-over response rate than the well-known individual CCPs components in our tests. Our current discovery demonstrates, for the first time, that integrating MLCT and conduction functional motifs in one structure is a useful, strategic design for enhancing the photodetecting performances of CCPs.

Results and Discussion

The single-crystal micro-flakes of **PhSeAg** were synthesized by a modification of previously reported method outlined in Figure 1 and Supporting Information

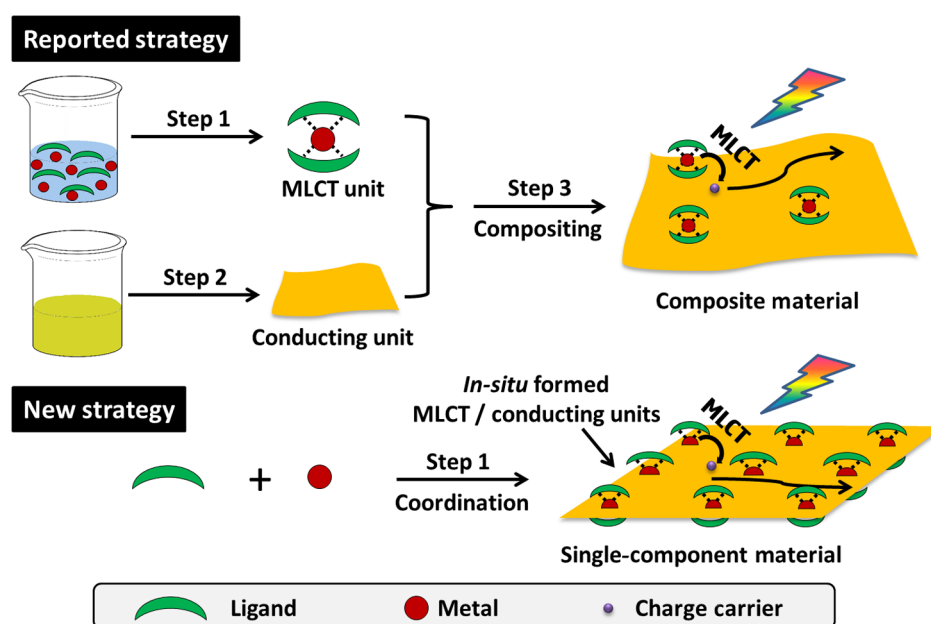


Figure 1 | Reported and our strategies for the preparation of MLCT-enhanced photodetecting materials.

Figures S1 and S2.¹⁴ The chemical and crystal structures of **PhSeAg** are shown in Figure 2a. Each Ag^+ coordinates with four Se atoms in a distorted AgSe_4 tetrahedron. AgSe_4 tetrahedrons are connected through sharing corners and edges to form a two-dimensional (2D) $\{\text{AgSe}\}_n$ inorganic layer. The phenyl rings connect to the Se atoms by covalent bonds, which are on both sides of the $\{\text{AgSe}\}_n$ layer. Hence, an organic/inorganic/organic sandwich-like structure is formed, with the layers stacking with each other by Van der Waals interaction to form a three-dimensional (3D) packing structure of **PhSeAg**.

Scanning electron microscopy image showed a sheet-like rhombic morphology of the prepared **PhSeAg**, which has lateral dimensions of tens of micrometers (Figure 2b) and thickness of several hundred nanometers (~ 200 – 500 nm) (inset of Figure 2b). The powder X-ray diffraction (PXRD; MiniFlex II, Rigaku, Japan) pattern of **PhSeAg** flakes (Figure 2c) was consistent with the simulated one, indicating the high purity and crystallinity nature of the flakes. The main diffraction peaks 002, 004, and 006 were assigned to the indexes of (001) crystal plane of **PhSeAg**. The UV-visible absorption spectra (Lambda 950, PerkinElmer, USA) of **PhSeAg** flakes (Figure 2d) showed strong absorption in the region of 200–480 nm, and a tail extended to 800 nm. The optical bandgap of **PhSeAg** measured was 2.57 eV (Supporting Information Figure S3).

The characterization of the nature of the excited states for a single **PhSeAg** crystal was performed by conducting femtosecond transient absorption (fs-TA; Ultrafast Systems, Helios Fire, USA) measurements for PhSeH in acetonitrile and **PhSeAg** in single-crystal form (Figure 3 and

Supporting Information Figure S4).¹⁵ PhSeH showed two evolution processes from 0.56 to 1.90 ps and 5.5 to 208 ps after excitation at a wavelength of ~ 267 nm (Supporting Information Figure S4A,B). The transient absorption (TA) spectra after 208 ps were assigned to the triplet state of PhSeH (Supporting Information Figure S4B).¹⁶ This assignment was confirmed further by a time-dependent density functional theory (TD-DFT) calculation, where the two apparent peaks centered at 410 and 475 nm matched well with the experimental TA spectra detected at 7.5 ns (Figure 3a). The nanosecond TA measurement (Figure 3b) revealed that the triplet state of PhSeH had a long lifetime of 8.4 μs .

The UV-vis absorption of **PhSeAg** in the range 200–450 nm, mainly contributed by the PhSe^- ligand because the solid-state of PhSeH also had a broad absorption band around 200–450 nm (see Supporting Information Figure S6). We unveiled the nature of the excited states between the PhSe^- ligands and Ag^+ centers in a single crystal by choosing three pump lasers with wavelengths of 400, 450, and 600 nm, respectively, to excite **PhSeAg**. The fs-TA spectra showed that **PhSeAg** excitation occurred at ~ 400 nm, similar to the behavior demonstrated by the excitation of PhSeH in acetonitrile by the laser at ~ 267 nm. **PhSeAg** experienced excitation in two stages (Supporting Information Figure S4D,E), as follows: the first stage was associated with the first singlet excited state of PhSe^- moiety of **PhSeAg**, attributable to the sharp transient peak observed at 478 nm within the whole molecule (Figure 3c). At later delay time, as the 478 nm value was very close to the shoulder TA of ~ 485 nm of the triplet state of PhSeH (Supporting

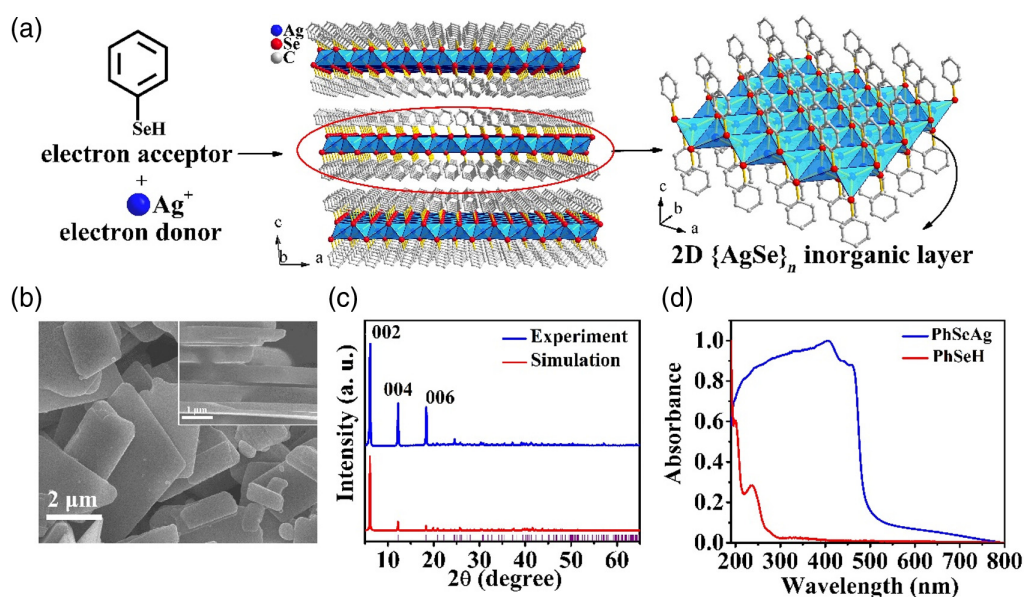


Figure 2 | Structure, morphology, and optical property of **PhSeAg**. (a) Synthetic route and the structure of **PhSeAg**. (b) Scanning electron microscopy SEM image and (c) experimental and simulated powder X-ray diffraction patterns of **PhSeAg** flakes. (d) UV-vis absorption spectra of **PhSeAg** in solid and PhSeH in acetonitrile.

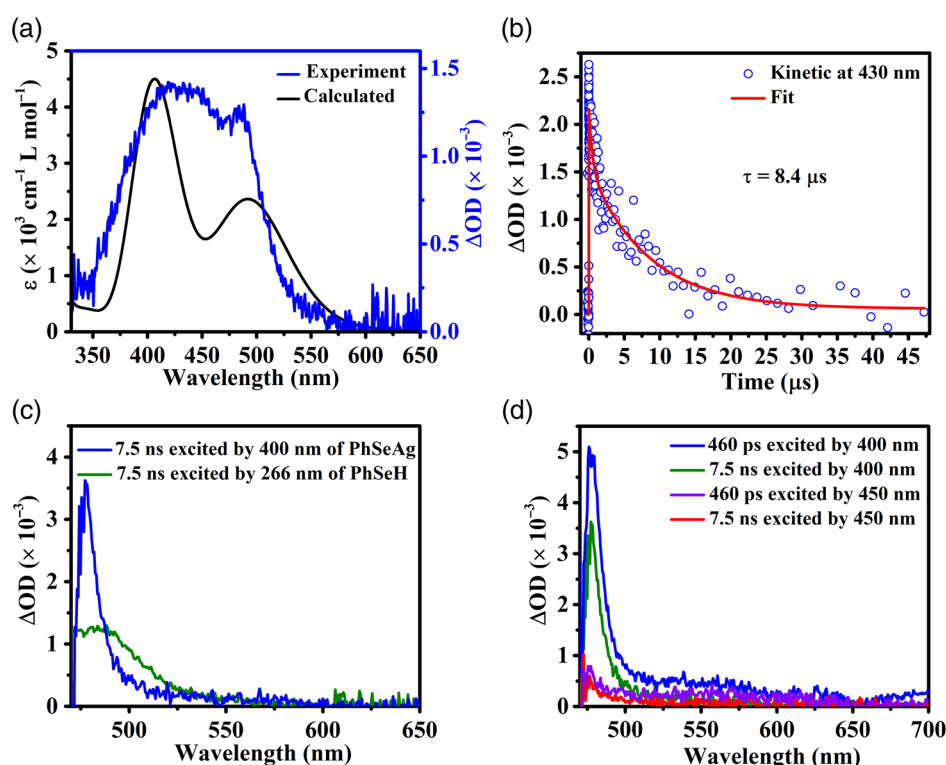


Figure 3 | Femtosecond transient absorption (fs-TA) measurements of PhSeAg and PhSeH. (a) Comparison between fs-TA at the delay time of 7.5 ns of PhSeH in acetonitrile pump by 267 nm and the UV-vis spectra obtained by time-dependent density functional theory calculations for a triplet of PhSeH. (b) Dynamics of the nanosecond TA of PhSeH at 430 nm in acetonitrile. (c) Comparison of the TA spectra at 7.5 ns of PhSeH and PhSeAg. (d) Comparison of the fs-TA spectra at 460 ps and 7.5 ns of PhSeAg pump by 400 and 450 nm, respectively.

Information Figure S4B), and the time constant (38 ps) of the second step for PhSeAg is almost the same with that of PhSeH (32 ps). Therefore, the second stage is convincingly assigned to the intersystem crossing (ISC) from the singlet excited state to the triplet state of ligand PhSe⁻. However, when the 450 nm pump laser was employed, the TA of **PhSeAg** was observed at 460 ps; as the excitation was increased to ~ 478 nm pump laser, there was an elimination of the time constant within the 460 ps (Figure 2d), which suggested the prompt quenching of the triplet state of the ligand PhSe⁻. We deduced that three possible processes might have led to the fast decay of TA at 478 nm as follows: (1) ligand-to-metal charge-transfer, (2) ligand-ligand annihilation, and (3) charge transfer between the ligand (PhSe⁻) and the metal (Ag⁺). When 400 nm pump laser was used, the triplet state of the ligand PhSe⁻ in **PhSeAg** exhibited no apparent decay, as the dynamic at 478 nm of **PhSeAg** was almost the same with that of the free PhSeH in acetonitrile. This revealed that ligand-to-metal charge-transfer and ligand-ligand annihilation processes could be ruled out. Besides, if only a d-d electronic transition among Ag⁺ ion took place, it should not affect the dynamics of PhSe⁻ ligand, and thus, the TA peak at 478 nm should not decay.

Nonetheless, in this instance, when the 450 and the 600 nm laser pumps were applied, the dynamics of PhSe⁻ ligand was dramatically shorter than the excitation produced by the 400 nm laser (Supporting Information Figure S4H), which suggested that a charge transfer had taken place between the ligand (PhSe⁻) and the metal (Ag⁺). Collectively, these findings provided evidence that only an MLCT process led to the fast decay of the excited state energy dynamics at 478 nm. Thereby, it is plausible for the charge transfer from the metal to the ligand to quench the TA quickly in the triplet state of PhSe⁻. The global fitting of the data matrix time constant of 5.6 ps was attributable to the MLCT process, consistent with the lifetime of MLCT reported in other systems.^{17,18} The lifetime of the recombination of MLCT obtained was 103 ps. Furthermore, the TA pumped by the 600 nm laser was very similar to that of the 450 nm excitation, indicating that the MLCT process took place when **PhSeAg** was excited by the light between 500 and 800 nm (for details see Supporting Information Figures S5 and S6). Interestingly, the time constant of 202 ps produced by the 600 nm pumped laser excitation, which was associated with the recombination of the MLCT process was longer than the 103 ps obtained by 450 nm excitation

(Supporting Information Figure S4F,G) of **PhSeAg**. Accordingly, the application of the 450 nm pump laser gained two-time constants (5.6 and 103 ps) that were different from the time constants pumped by 400 nm laser of the first ion. This suggested that the charge carriers pumped by the laser at 600 nm were more favorable for the charge transport in the inorganic layer.

The electrical properties of the **PhSeAg** powder pellet were studied by a direct current two probe method using the semiconductor characterization system (4200SCS, Keithley, USA; Figure 4a).^{19–21} The conductivity of **PhSeAg** increased three orders of magnitude, that is, from 2.93×10^{-11} to 3.95×10^{-8} S cm⁻¹ in the range of 308–418 K, which indicated its typical semiconductive characteristic. With temperature increments (308–418 K), the exponential conductivity (σ) varied with $\exp(-E_a/kT)$ (E_a is the activation energy), which suggested that **PhSeAg** possessed a thermal-activated band-like transport (Figure 4b).¹⁹ The density functional theory (DFT) calculation revealed that the **PhSeAg** possessed a direct bandgap structure, and the valence band maximum (VBM) at the Gamma (G) point was constructed mainly by the orbitals of the metal cation (Ag⁺) and the Se atoms (Figure 4c,d). These results suggested that the benzene groups in **PhSeAg** were bonded covalently to the inorganic layers, and therefore, the charge carriers transport mainly in the inorganic layer.

The large bandgap (>2.0 eV) of wide bandgap semiconductors limits their application in the visible range.^{22–24} We considered that the MLCT of **PhSeAg** in the whole visible-light range might extend its response spectra range. The single-crystal **PhSeAg** flake was placed on Si/SiO₂ substrate with pre-prepared Cr/Au parallel electrodes with an effective device area of 30 μm^2 for photodetection (Figure 5a). Monochromatic lights with different wavelengths were each applied as light sources. The inset of Figure 4b shows the typical *I*-*V* curves under dark and white light. Figure 5b exhibits a wavelength-dependent responsivity (R_λ) of **PhSeAg** from 400 to 800 nm. The optimum responsivity of **PhSeAg** was in agreement with its MLCT induced strong absorption at the wavelength of 500 nm. Interestingly, although the MLCT induced absorption in 500–700 nm is much weaker than the absorption of the ligand in the range of 300–450 nm (Figure 2d), the responsivity at 600 nm was unexpectedly stronger than that at 400 nm. Even at 700 nm, which is almost the end of the absorption tail, the responsivity was still comparable with that at 400 nm. These observations demonstrated that the MLCT generated by the **PhSeAg** was an effective process that resulted in producing a strong photocurrent and also extended the spectral range of the photoresponse.

To reveal the photodetecting performances in more detail, **PhSeAg** was studied with 500 nm light

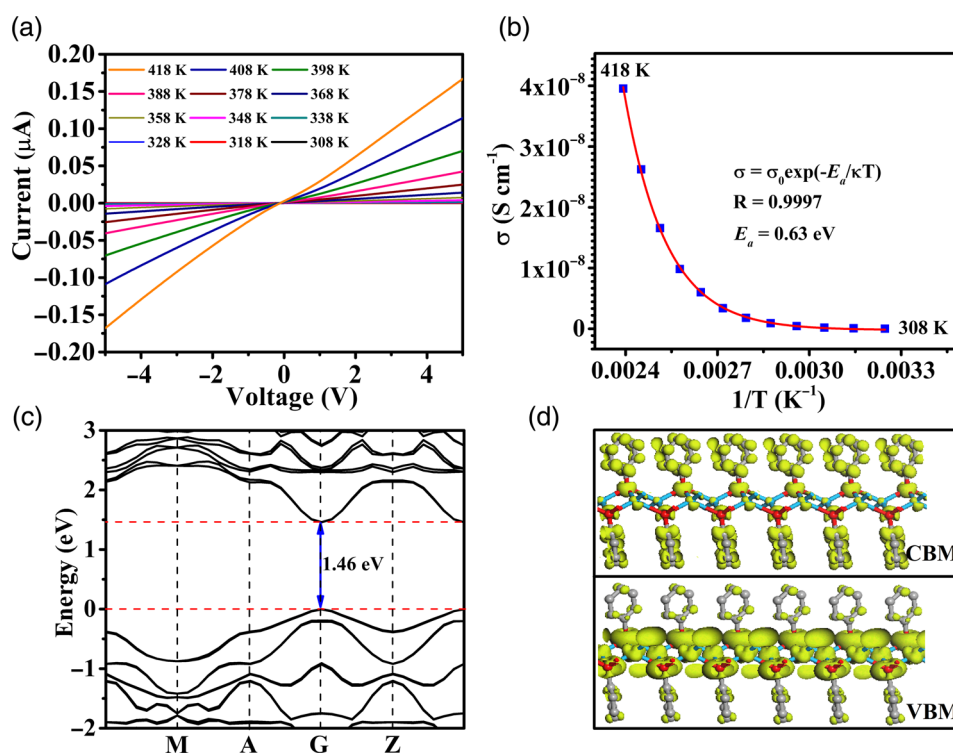


Figure 4 | Electrical properties of the **PhSeAg**. (a) Temperature-dependent *I*-*V* curves of **PhSeAg**. (b) Arrhenius plots of conductivity of **PhSeAg**. (c) Band structure of **PhSeAg**. (d) Valence band maximum and conduction band minimum of **PhSeAg** at Gamma (G) point.

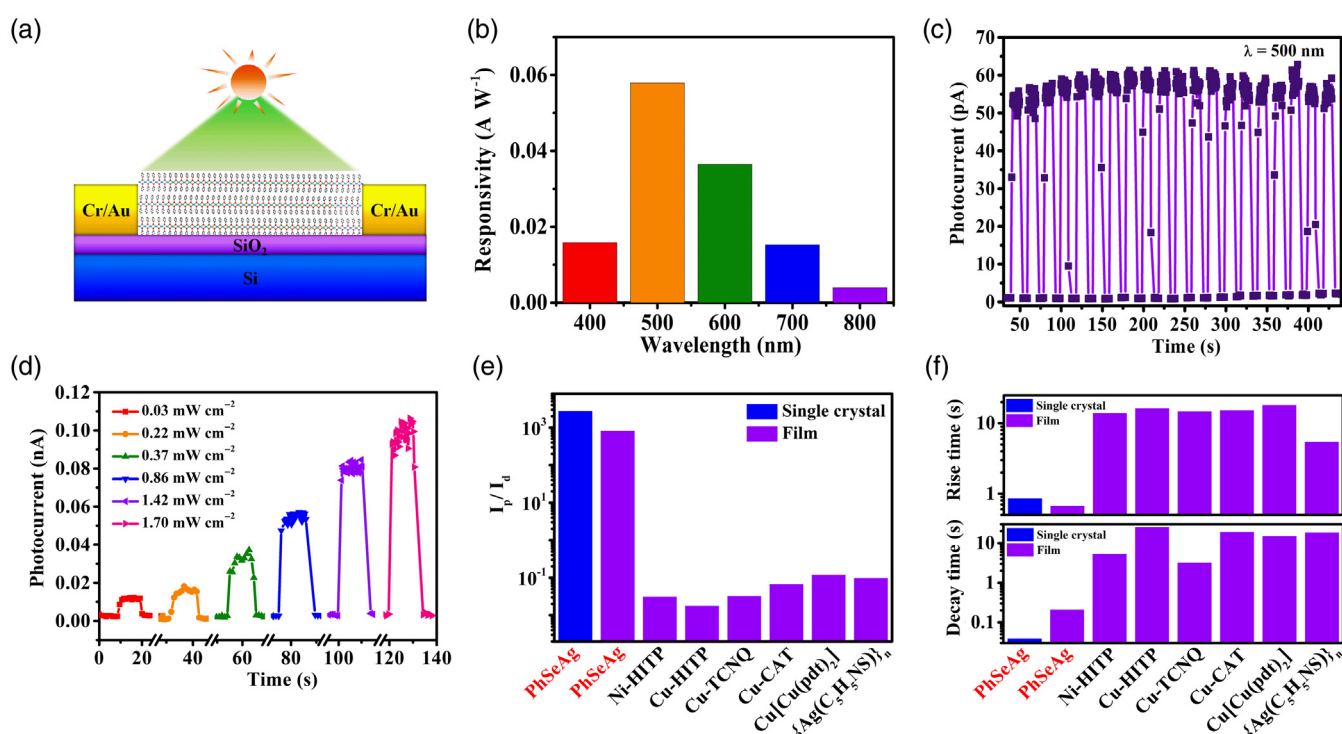


Figure 5 | Photodetection measurements of PhSeAg. (a) Schematic diagram of **PhSeAg** single-crystal-based photodetector. (b) Responsivities versus light absorption of **PhSeAg** at different wavelengths, insets are the I–V curves and the optical image of **PhSeAg** single-crystal-based photodetector. (c) Time-dependent photoresponse of **PhSeAg** under periodic illumination. (d) Photoresponse of **PhSeAg** flake under illumination with different light intensities. (e) Comparison of the on/off ratio and (f) rise time and decay time of different coordination polymers.

illumination with a fixed power of 1.70 mW cm⁻². As shown in Figure 5c, **PhSeAg** exhibited an alternative on/off photocurrent with a ratio of nearly two orders of magnitude when irradiated by the periodic light pulses. Additionally, the on/off switching behavior of **PhSeAg** could be well retained for 20 cycles with negligible decay, indicating its good repeatability and long-term cycling stability. Based on a high-resolution on/off scan, the response time (τ_{rise}) and decay time (τ_{decay}) were deduced as 0.94 and 0.045 s, respectively (Supporting Information Figure S7). Also, the R_{λ} and detectivity (D^*) were calculated to be 0.119 A W⁻¹ and 1.29×10^{11} Jones, respectively, at a bias of 2 V. Light-intensity-dependent optoelectronic properties of **PhSeAg** were also studied. We found that **PhSeAg** could generate an apparent photocurrent even when illuminated with an optical power as low as 0.03 mW cm⁻² (Figure 5d), indicating its high sensitivity. The R_{λ} and D^* of **PhSeAg** increased slightly as the light intensity decreased (Supporting Information Figure S8).

According to the fs-TA measurements, the photoexcited electrons were transferred and located at the organic ligand through MLCT, which significantly enhanced the generation and separation of the photoexcited charge carrier. Moreover, different from the isolated inorganic nodes in common CCPs, the continuous metal

chalcogenides layer in **PhSeAg** was favorable for the fast transportation of carriers. The optoelectrical properties of a crystallite thick film of **PhSeAg** and the various well-known CCPs were compared. The **PhSeAg** film showed two orders of magnitude higher on/off ratio and one order of magnitude shorter for τ_{rise} and τ_{decay} , respectively (Figure 5e,f and Supporting Information Figures S9–S11). The **PhSeAg** film also showed superior performances, including on/off ratio, rise and decay time, than other reported CCPs (Supporting Information Table S1).

Conclusion

In this report, the fabrication of a single-component MLCT photodetecting material (CCP-**PhSeAg**) was achieved for the first time. The prepared CCP-**PhSeAg** material adopted a continuous conducting {AgSe}_n layered structure, which provided a smooth electron transport route, whereas the organic functional groups on {AgSe}_n layers afforded matched energy levels with the inorganic layer of MLCT. The MLCT processes, revealed by fs-TA measurements, significantly enhanced the generation and separation of charge carriers under irradiation. Due to its strong MLCT capabilities, **PhSeAg** showed response to whole visible-light range, the ultrahigh sensitivity to weak light (0.03 mW cm⁻²), highest on/off

current ratio, and fastest response speed than the well-known CCPs. Since MLCT processes could be rationally achieved in coordination polymers, our work indeed provides a new versatile strategy for the optoelectronic enhancement of the properties of CCPs.

Supporting Information

Supporting Information is available.

Conflict of Interest

The authors declare that they have no conflict of interests.

Acknowledgments

This work was supported by the NSF of China (21822109, 21805276, 21773245, 21773151, 21975254), National Key R&D Program of China (2017YFA0206802), the Strategic Priority Research Program of Chinese Academy of Sciences (XDB20000000), Key Research Program of Frontier Science, Chinese Academy of Sciences (QYZDB-SSW-SLH023), Youth Innovation Promotion Association CAS, International Partnership Program of CAS (121835KYSB201800).

References

- Elahi, S. M.; Chand, S.; Deng, W. H.; Pal, A.; Das, M. C. Polycarboxylate-Templated Coordination Polymers: Role of Templates for Superprotonic Conductivities of up to 10^{-1} S cm $^{-1}$. *Angew. Chem. Int. Ed.* **2018**, *57*, 6662–6666.
- Otsubo, K.; Haraguchi, T.; Kitagawa, H. Nanoscale Crystalline Architectures of Hofmann-Type Metal–Organic Frameworks. *Coord. Chem. Rev.* **2017**, *346*, 123–138.
- Zhao, M.; Huang, Y.; Peng, Y.; Huang, Z.; Ma, Q.; Zhang, H. Two-Dimensional Metal–Organic Framework Nanosheets: Synthesis and Applications. *Chem. Soc. Rev.* **2018**, *47*, 6267–6295.
- Jiang, D.; Chen, M.; Wang, H.; Zeng, G.; Huang, D.; Cheng, M.; Liu, Y.; Xue, W.; Wang, Z. The Application of Different Typological and Structural MOFs-Based Materials for the Dyes Adsorption. *Coord. Chem. Rev.* **2019**, *380*, 471–483.
- Pan, M.; Liao, W. M.; Yin, S. Y.; Sun, S. S.; Su, C. Y. Single-Phase White-Light-Emitting and Photoluminescent Color-Tuning Coordination Assemblies. *Chem. Rev.* **2018**, *118*, 8889–8935.
- Wang, F.; Wang, Z. X.; Yin, L.; Cheng, R. Q.; Wang, J. J.; Wen, Y.; Shifa, T. A.; Wang, F. M.; Zhang, Y.; Zhan, X. Y.; He, J. 2D Library Beyond Graphene and Transition Metal Dichalcogenides: A Focus on Photodetection. *Chem. Soc. Rev.* **2018**, *47*, 6296–6341.
- Gong, C. H.; Hu, K.; Wang, X. P.; Wang, P. H.; Yan, C. Y.; Chu, J. W.; Liao, M.; Dai, L. P.; Zhai, T. Y.; Wang, C.; Li, L.; Xiong, J. 2D Nanomaterial Arrays for Electronics and Optoelectronics. *Adv. Funct. Mater.* **2018**, *28*, 1706559.
- Wang, H.; Kim, D. H. Perovskite-Based Photodetectors: Materials and Devices. *Chem. Soc. Rev.* **2017**, *46*, 5204–5236.
- Karabulut, A.; Dere, A.; Dayan, O.; Al-Sehemi, A. G.; Serbetci, Z.; Al-Ghamdi, A. A.; Yakuphanoglu, F. Silicon Based Photodetector with Ru(II) Complexes Organic Interlayer. *Mater. Sci. Semicond. Process.* **2019**, *91*, 422–430.
- Ren, X. C.; Yang, F. X.; Gao, X.; Cheng, S. S.; Zhang, X. T.; Dong, H. L.; Hu, W. P. Organic Field-Effect Transistor for Energy-Related Applications: Low-Power-Consumption Devices, Near-Infrared Phototransistors, and Organic Thermoelectric Devices. *Adv. Energy Mater.* **2013**, *8*, 1801003.
- Whittemore, T. J.; White, T. A.; Turro, C. New Ligand Design Provides Delocalization and Promotes Strong Absorption Throughout the Visible Region in a Ru(II) Complex. *J. Am. Chem. Soc.* **2018**, *140*, 229–234.
- Liu, X.; Lee, E. K.; Oh, J. H. Graphene–Ruthenium Complex Hybrid Photodetectors with Ultrahigh Photore-sponsivity. *Small* **2014**, *10*, 3700–3706.
- Liu, X.; Lee, E. K.; Kim, D. Y.; Yu, H.; Oh, J. H. Flexible Organic Phototransistor Array with Enhanced Responsivity via Metal–Ligand Charge Transfer. *ACS Appl. Mater. Inter-faces* **2016**, *8*, 7291–7299.
- Cuthbert, H. L.; Wallbank, A. I.; Taylor, N. J.; Corrigan, J. F. Synthesis and Structural Characterization of [Cu₂₀Se₄(μ₃-SePh)₁₂(PPh₃)₆] and [Ag(SePh)]_∞. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2483–2488.
- Huang, J.; Buyukcakir, O.; Mara, M. W.; Coskun, A.; Dimitrijevic, N. M.; Barin, G.; Kokhan, O.; Stickrath, A. B.; Ruppert, R.; Tiede, D. M.; Stoddart, J. F.; Sauvage, J. P.; Chen, L. X. Highly Efficient Ultrafast Electron Injection from the Singlet MLCT Excited State of Copper(I) Diimine Complexes to TiO₂ Nanoparticles. *Angew. Chem. Int. Ed.* **2012**, *51*, 12711–12715.
- Riyad, Y. M. Thioanisole Triplet: Laser Flash Photolysis and Pulse Radiolysis Studies. *J. Photochem. Photobiol. A: Chem.* **2017**, *335*, 294–299.
- Zhong, F.; Zhao, J.; Hayvali, M.; Elmali, A.; Karatay, A. Effect of Molecular Conformation Restriction on the Photo-physical Properties of N⁴N Platinum(II) bis(ethynyl)naphtha-limide) Complexes Showing Close-Lying ³MLCT and ³LE Excited States. *Inorg. Chem.* **2019**, *58*, 1850–1861.
- Jiang, C. C.; Young, P. J.; Xu, S. B.; Gallucci, J. C.; Chisholm, M. H. Femtosecond Study of Dimolybdenum Paddlewheel Compounds with Amide/Thioamide Ligands: Symmetry, Electronic Structure, and Charge Distribu-tion in the ¹MLCT S₁ State. *Inorg. Chem.* **2017**, *56*, 1433–1445.
- Wang, G. E.; Xu, G.; Liu, B. W.; Wang, M. S.; Yao, M. S.; Guo, G. C. Semiconductive Nanotube Array Constructed from Giant [Pb¹⁸I₅₄(I₂)₉] Wheel Clusters. *Angew. Chem. Int. Ed.* **2016**, *55*, 514–518.
- Sun, L.; Park, S. S.; Sheberla, D.; Dincă, M. Measuring and Reporting Electrical Conductivity in Metal–Organic Frame-works: Cd₂(TTFB) as a Case Study. *J. Am. Chem. Soc.* **2016**, *138*, 14772–14782.

21. Le Ouay, B.; Boudot, M.; Kitao, T.; Yanagida, T.; Kitagawa, S.; Uemura, T. Nanostructuration of PEDOT in Porous Coordination Polymers for Tunable Porosity and Conductivity. *J. Am. Chem. Soc.* **2016**, *138*, 10088–10091.
22. Yan, F.; Xin, X.; Aslam, S.; Zhao, Y.; Franz, D.; Zhao, J. H.; Weiner, M. 4H-SiC UV Photodetectors with Large Area and Very High Specific Detectivity. *IEEE J. Quantum Electron.* **2004**, *40*, 1315–1320.
23. Zou, Y.; Zhang, Y.; Hu, Y.; Gu, H. Ultraviolet Detectors Based on Wide Bandgap Semiconductor Nanowire: A Review. *Sensors* **2018**, *18*, 2072.
24. Lu, Y. J.; Lin, C. N.; Shan, C. X. Optoelectronic Diamond: Growth, Properties, and Photodetection Applications. *Adv. Optical Mater.* **2018**, *6*, 1800359.