Concerted Photoluminescence of Electrochemically Self-Assembled CuSCN/Stilbazolium Dye Hybrid Thin Films

Kyota Uda,† Yuki Tsuda,† Shuji Okada,† Ryohei Yamakado,† Lina Sun,† Yoshiyuki Suzuki,† Matthew Schuette White,‡ Madalina Furis,† Philipp Stadler,§ Oleg Dimitriev,∥ and Tsukasa Yoshida*†

†Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan
‡Department of Physics, University of Vermont, Burlington, Vermont 05405, United States
§V. Lashkaryov Institute of Semiconductor Physics, National Academy of Science of Ukraine, pr. Nauki 45, Kiev 03028, Ukraine
∥Institute of Physical Chemistry, Johannes Kepler University Linz, Altenbergerstrasse 69, 4040 Linz, Austria

ABSTRACT: Hybrid thin films of crystalline CuSCN and 4-(N,N-dimethylamino)-4′-(N-methyl)stilbazolium (DAS) in three distinctively different nanostructures were obtained by electrochemical self-assembly from a single pot containing all the chemical ingredients. Their optical properties for UV–vis-NIR absorption, photoluminescence (PL), and PL excitation spectra were examined between 77 and 298 K, in comparison with solution and solid powder of DAS tosylate (DAST). Unlike all other dyes we tested before, PL of DAS was not quenched but rather enhanced when hybridized with CuSCN. DAST exhibited a strong exciton–phonon coupling to weaken, broaden, and red shift PL at room temperature, so that it inversely is strongly enhanced, sharpened, and blue-shifted at 77 K. The PL of the same dye in the hybrid thin film, however, shows a slight red shift and only a moderate enhancement at reduced temperatures due to strong exciton stabilization in dielectric environment of CuSCN and concerted PL by energy transfer from CuSCN to DAS luminophore, making it a unique nearly temperature-independent luminescent material.

INTRODUCTION

Combination of inorganic and organic materials offers unlimited opportunities in the synthesis of new materials. Whereas “composites” typically stands for their physical mixtures to exploit physical properties of each component together, such as carbon fiber reinforced plastics, “hybrids” and “inorganic/organic compounds” are especially interesting for concerted new functionalities expected from intimate interaction between inorganic and organic constituents, since they are combined together by self-assembly due to favorable “chemistry” between them.

We have previously established a method to electrochemically self-assemble (ESA) inorganic/organic hybrid thin films.1–5 When organic molecules with certain anchoring groups are added to the baths for cathodic electrodeposition of inorganic compound thin films, and when there is a right chemistry between the added molecule and the inorganic compound to be deposited, ESA of nanostructured hybrid thin film spontaneously occurs. For example, organic dye molecules bearing a carboxylic acid group such as Eosin Y undergoes ESA with ZnO when they are added to aqueous ZnCl₂ bath saturated with O₂,5–8 whereas many cationic dyes afford hybrid thin films during cathodic electrodeposition of CuSCN by replacing a part of Cu⁺ ions.9,10 Wrong combination such as that adding Eosin Y to the bath for CuSCN electrodeposition, namely, alcoholic solutions containing Cu²⁺ and SCN⁻ ions, did not yield hybrid thin films, indicating strict selectivity in ESA.5,11

The strong interaction between inorganic and organic constituents to achieve ESA in return lets us anticipate concerted new functionalities. The leading example is the photoelectrochemical charge separation used in dye-sensitized solar cells.12 Photoexcited organic dye molecules bound to the surface of inorganic semiconductors inject either electron or hole to the conduction band of n-type metal oxide2,4,12,13 or to the valence band of p-type materials such as NiO14 or CuSCN,9,15,16 respectively, when the energy levels of the constituents are matched. Such light-induced charge separation has also been observed for the hybrid thin films by ESA in their solid states. The fluorescence of Eosin Y was completely quenched for the ZnO/Eosin Y hybrid thin film by ESA7 and a color-selective photoconductor could be achieved with this...
material owing to the photocarrier generation.\textsuperscript{13} Likewise, total quenching of fluorescence was also observed for the CuSCN/dye hybrid thin films by ESA with highly fluorescent dyes such as rhodamine B (RB) and Nile blue A.\textsuperscript{17} Indeed, dye-sensitized photocathodic current was observed for a porous CuSCN sensitized with RB.\textsuperscript{9}

A totally contrasting concerted photophysical functionality has been discovered for CuSCN hybrid thin films with 4-(\textit{N},\textit{N}-dimethylamino)-4’-(\textit{N’}-methyl)stilbazolium (DAS) and is reported in this paper. ESA of CuSCN/DAS hybrid thin films has successfully been achieved and established by the addition of DAS tosylate salt (DAST, Figure 1) into the bath for electrodeposition of CuSCN.\textsuperscript{10} DAST crystal is known for its nonlinear optical (NLO) properties owing to the ordered alignment of the strong dipole of DAS cations, exhibiting special functionalities such as frequency-modulation for terahertz generation\textsuperscript{18–20} and two-photon excited fluorescence upconversion.\textsuperscript{21,22}

Unlike all other fluorescent dye molecules we tested before, the present CuSCN/DAS hybrid thin films have been found to exhibit strong fluorescence from the DAS luminophore enhanced by the CuSCN host. Highly polar environment of inorganic CuSCN can favor ordering of DAS during the ESA. In fact, we have achieved hybrid thin films in three distinctively different structures out of the same materials combination, simply by tuning DAST concentration in the deposition bath.\textsuperscript{10} Their photoluminescence (PL) properties have been examined in a temperature range between 77 and 298 K, and in comparison with those of DAST and CuSCN, to elucidate the origin of the concerted photoluminescence.

\section*{RESULT AND DISCUSSION}

Cathodic electrodeposition of CuSCN thin films has already been well established and understood.\textsuperscript{9,11,16,23} A 1:1 complex between Cu\textsuperscript{2+} and SCN\textsuperscript{−} ions, denoted as [Cu(SCN)]\textsuperscript{+}, is spontaneously formed by dissolving equal molar amounts of Cu(ClO\textsubscript{4})\textsubscript{2} and LiSCN in alcohol such as methanol and ethanol. This complex is the active species to be reduced at the electrode to precipitate CuSCN with a Faradic efficiency of practically 100%.\textsuperscript{16,23}

\[ [\text{Cu(SCN)}]^{+} + e^{-} \rightarrow \text{CuSCN} \]  \hspace{1cm} (1)

Since charge transfer is fast, this reaction is solely limited by the transport of [Cu(SCN)]\textsuperscript{+} even in the presence of dyes to hybridize.\textsuperscript{23,24} For this reason, we employ a rotating disk electrode (RDE) to control mass transport by homogeneous forced convection. Thus, highly homogeneous and well-adherent thin films can be obtained in a reproducible manner.

The pure CuSCN thin film without the addition of DAST is made of particles with smooth surface in 100–200 nm size (Figure 2a), crystallized into rhombohedral β-CuSCN.\textsuperscript{10}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Structure of DAST.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Scanning electron microscope pictures of the electrodeposited film samples: pure CuSCN without DAST (a), CuSCN/DAS hybrid thin films by ESA from baths containing DAST at 25 \textmu mol dm\textsuperscript{-3} (b) (DAS occluded in β-CuSCN), 250 \textmu mol dm\textsuperscript{-3} (c) phase-separated β-CuSCN/DAS in a haircomb nanostructure, and 1000 \textmu mol dm\textsuperscript{-3} (d) phase-separated α-CuSCN/DAS in a scale nanostructure.}
\end{figure}

Increasing addition of DAST in the deposition bath results in drastic changes of the morphology, crystal orientation/structure, and dye loading.\textsuperscript{10} With the minor addition at 25 \textmu mol dm\textsuperscript{-3}, DAS is “occluded” inside of β-CuSCN grains.\textsuperscript{10} Although some roughness is recognized on its surface (Figure 2b), it was not possible to dissolve away DAS by soaking this film in dimethylacetamide (DMA), which is a good solvent of DAS but poor for CuSCN, so the film remained intact.\textsuperscript{10} At 250 \textmu mol dm\textsuperscript{-3}, a unique “haircomb” nanostructure appears (Figure 2c). It has previously been found that the teeth of the haircomb are oriented along the c-axis of β-CuSCN and DAS precipitated in large amount is phase separated to fill out the gap between the teeth, so that an interdigitated inorganic/organic hybrid nanostructure is spontaneously formed. As the organic moiety is segregated from CuSCN, soaking this film in DMA results in a total extraction of DAS to leave the CuSCN haircomb.\textsuperscript{10} The transition from occluded to haircomb hybrid structures is quantitatively understood, as it is caused by the switching of dye-loading mechanism.\textsuperscript{24} With low DAST concentration, the loading of DAS is diffusion limited, so that all the DAS ions reaching the electrode surface are buried inside the CuSCN grain. When DAST concentration is high, surface reaction of hybridization limits the loading to allow structural re-organization into the unique phase-separated nanostructure.\textsuperscript{10} With an extreme high addition of DAST at 1000 \textmu mol dm\textsuperscript{-3}, the film morphology changes once again into a “scale”-like nanostructure (Figure 2d). CuSCN in fact changes from the β-form into monoclinic α-CuSCN.\textsuperscript{10} The space between the interconnected nanoplatelets is filled with DAS, so that its lamellar structure becomes apparent when soaked in DMA.\textsuperscript{10} The reason for the transition from haircomb to scale is presently unknown and is a subject of our study. What has been shown and documented here is the fact that we can produce CuSCN/DAS hybrid nanostructures in three distinctively different forms out of the same components, which then are very interesting samples to be compared.

Figure 3 compares the UV–vis–NIR absorption, photoluminescence (PL), and PL excitation (PLE) spectra measured...
samples.

could not be overcome even by reducing the excitation power reduces the PL energy toward the NIR range. The PLE showing its peak around 720 nm. Exciton head-to-tail interaction caused by ordering of the DAS wavelength to create a shoulder around 590 nm, due to J-type delocalize exciton within the DAST crystal signifi- 

powder is signi- 

transmission, whereas in di- 

ff 

nm) measured at 298 K. The absorption spectra were measured in the solution, unlike the DAST powder that shows broadening slightly shifted and broadened strictly toward red from that of the solution and powder of the DAST sample. The peak is samples are compared, their energy appears between those of the absorption spectrum.

onset wavelengths, which are matched with those of the PLE spectra, showing an abrupt large red shift of the peak wavelength to decrease the Stokes shift down around 680 nm right between them, indicating its own energetic structure. We are unable to quantify the efficiency of PL in the present setup that typically measures for excitation beam incidence at 60° and monitoring at 30° with respect to the plane of the film and powder samples to avoid direct reflection of the excitation beam. Because each sample has rather different optical density and reflectivity, total absorption and emission need to be measured by employing an integration sphere for the calculation of PL quantum yields to achieve strict comparison. However, strong PL intensity was monitored for the hybrid film samples despite their limited optical density and specular reflection as compared to the DAST powder that has infinitely large optical density and a totally matt appearance (see the Supporting Information for comparison of PL spectra intensity measured for the same slit width).

To scrutinize the PL properties of DAST, temperature dependence of PL and PLE has been examined in a temperature range between 77 and 298 K both for its solution in methanol and its solid powder (Figure 4). The PL of DAS in methanol is significantly enhanced with decrease of temper- 
ature owing to suppressed nonradiative decay by TICT. Moreover, the PL energy abruptly shifts from about 610−580 nm between 200 and 150 K upon freezing of the solvent methanol (melting point = 176 K). These changes coincide with those of the PLE spectra, showing an abrupt large red shift of the peak wavelength to decrease the Stokes shift down to ca. 50 nm at 77 K. The freezing of the molecular twisting motion makes the chromophore planar to reduce the HOMO−lowest unoccupied molecular orbital energy gap. On the other hand, the solid DAST shows strong enhance- 
ment, sharpening, and blue shift of PL upon decrease in temperature. Comparison of the PL spectra between 77 and 298 K clearly shows the sharpening and blue shift of the peak wavelength as much as 60 nm due to suppressed exciton delocalization within the DAST crystals. The PLE spectra once again are rather featureless, but begin to show a clear peak at around 610 nm upon reduction of temperature. These strong enhancement, sharpening, and blue shift of the PL peaks for the DAST samples on decrease in temperature were well- 
expected and simple to understand as consequences of suppressed exciton relaxation to reduce its loss by thermal- 
ization.

Finally, temperature-dependent PL and PLE spectra were examined for three different kinds of DAST/DAS hybrid thin films prepared by ESA (Figure 5). All of them exhibit PL clearly originating from DAS, but their energy differ from one to the other with different peak wavelengths and shapes of the
differed. First, it should be reminded with emphasis that DAS is the first and only example to show PL when hybridized with CuSCN, so far as our experiences are concerned. All other dyes we tested underwent total quenching of fluorescence. Since highest occupied molecular orbital (HOMO) of DAS has been estimated as −5.48 eV (vs VAC), well below the valence band edge of CuSCN (−5.3 eV), the hole injection from photoexcited DAS to CuSCN could very well be expected from the energy alignment point of view.

DAS adsorbed on CuSCN powder emits just like the monomer in a solution, showing a sharp peak, which, in fact, is slightly blue-shifted to around 600 nm. It is likely that the relaxation by TICT is suppressed within the densely adsorbed DAS layer. On the contrary, the PL spectrum of the hybrid thin film by ESA is clearly broader than that of the DAST solution but narrower than that of the powder, with its peak around 680 nm right between them, indicating its own energetic structure.
spectra, indicating differences of the environments for the DAS luminophore in these films. The PL intensity is enhanced for all the samples upon decrease in temperature but to a much lesser extent than those of the solution and powder of DAST. Especially, the haircomb hybrid shows only a marginal increase with less than 2 times enhancement compared between 77 and 298 K (Figure 5b). The remarkable finding is the slight "red-shift" of the PL peaks for all the samples, which clearly contrary to the behavior of DAST solution and solid. The broadening of the PL peaks of the hybrid thin films suggests the delocalization of exciton within DAS aggregates, which should be present in these samples, rather than emission from molecularly confined exciton. Dielectric environment of the surrounding CuSCN seems to result in a strong stabilization of exciton in DAS aggregates and the differences of the hybrid structure result in different degrees of interaction to cause observed differences of the PL behavior for the three kinds of CuSCN/DAS hybrid thin films. At present, we are unable to comment on the difference of absolute quantum yields of PL from these hybrid films, also with respect to those of the solution and solid of DAST, since optical density differs from film to film.10 The higher DAST concentration for electro-deposition results in the higher DAS content in the film, so that the PL intensity at room temperature appeared in the order as scale > haircomb > occluded (see the Supporting Information), although total emission based on total absorption needs to be compared by measuring them with an integration sphere to talk about their PL efficiencies. For all these films, however, rather temperature-independent PL obviously speaks for suppressed thermalization loss of exciton. Also, the independence of the Stokes shift on temperature indicates suppressed vibronic motion of DAS in the hybrids.

The PLE spectra of the hybrid thin films indicate the main contribution of direct IMCT photoexcitation of DAS as all of them show high intensities between 450 and 600 nm, matched with the absorption spectra of the samples. However, the spectra become rather distorted at reduced temperatures, especially for the scale α-CuSCN/DAS hybrid (Figure 5c), showing a prominent sharp peak at 380 nm and another double peak in the range between 400 and 450 nm at 77 K. Similar distortion is actually observed to smaller degrees for the haircomb (Figure 5b) and occluded (Figure 5a) hybrids. None of them, however, show such features in their absorption spectra, so that some accounts need to be made for these additional peaks in the PLE.

We then checked the PL spectra for the pure β-CuSCN thin film electrodeposited without DAST, β-CuSCN powder, and also the precursor solution for the electrodeposition of CuSCN, namely, [Cu(SCN)]+ in methanol (Figure 6). Even though apparently rather weak, the broad emission peak for CuSCN thin film appeared at around 826 nm. The CuSCN powder also exhibited a broad emission even weaker and in a shorter wavelength range than the electrodeposited film. Then,
acceptor levels in its SCN made it most e
Since the energy transfer event is expected at the interface band-edge absorption (380 nm) and LMCT absorption (400−450 nm) at the surface results in enhanced concerted PL from CuSCN for its band gap of around 3.4 eV. Because of the energy transfer event is expected at the interface band-edge absorption to which SCN ions are bound. On the other hand, the sharp peak at 380 nm in the PLE can be associated with the band-edge absorption of CuSCN (Figure 5), although these peaks at 380 and 400−450 nm range are not recognized in its absorption spectrum. The PLE of the powder sample shows a broad peak centered at about 420 nm, which is also not seen in the PLE spectrum. The PLE of the CuSCN/DAS hybrid thin films with respect to variation of their composition and nanostructure is therefore an exciting challenge in future.

CONCLUSIONS

Optical properties of CuSCN/DAS hybrid thin films prepared by ESA were examined. Unlike many other dye molecules we tested before, the fluorescence of DAS was not quenched but rather enhanced when hybridized with CuSCN. Dielectric environment as well as ordered alignment of DAS by CuSCN greatly stabilizes the exciton against thermalization loss by suppressing TICT and exciton−phonon coupling. Unlike DAST solution and solid powder, PL of the CuSCN/DAS hybrid thin films was much less enhanced on decreasing the temperature, associated with a slight red-shift of the emission energy. The smallest temperature dependence, thus to be interpreted as the strongest exciton stabilization, was found for the haircomb β-CuSCN/DAS hybrid.

EXPERIMENTAL SECTION

Tosylate salt of 4-(N,N-dimethylamino)-4′-(N′-methyl)-stilbazolium (DAST) was synthesized according to the procedure described in literature. CuSCN powder was purchased from TCI and used as received. It was also modified by adsorbing DAS by putting 250 mg of CuSCN into 250 μmol dm−3 DAST solution in methanol and stirring overnight at room temperature.

We have previously reported details of ESA of CuSCN/DAS hybrid thin films. In this study, we have employed a methanol (Wako) containing 2.5 mmol dm−3 Cu(ClO4)2 (Sigma-Aldrich), 2.5 mmol dm−3 LiSCN (Kishida), and 0.1 mol dm−3 LiClO4 (Wako, supporting electrolyte) as the bath for potentiostatic (+0.2 V vs Ag/AgCl) cathodic electrode-deposition of CuSCN (under air, 298 K) for 180 s, according to the diffusion-limited reduction of 1:1 complex between Cu2+ and SCN− ions, described as eq 1. F-Doped SnO2-coated conductive glass (Asahi-DU, 10 Ω sq−1) used as the substrate was furnished into a rotating disk electrode (RDE, diameter = 500 μm) used as the substrate was furnished into a rotating disk electrode (RDE, diameter = 500 μm) at 1.1 V, 0.5 V, and 0.0 V, respectively, and the solutions were stirred at 1000 rpm. DAST was dissolved at various concentrations of 25, 250, and 1000 μmol dm−3 of the bath to promote ESA of hybrid thin films. Surface morphology of the electrodeposited thin films was observed by JEOL JSM-6700F field emission scanning electron microscope.

UV−vis−NIR absorption spectra were measured on a SHIMADZU SolidSpec-3700 spectrophotometer in transmission (solutions and thin films) and diffuse reflection (powder samples) employing an integration sphere. Photo-luminescence (PL) and PL excitation (PLE) spectra were measured on a HORIBA Fluorolog-3 equipped with a high-power Xe lamp excitation source and DAp.
cooled photomultiplier tube (PMT) detector in a temperature range between 77 and 298 K employing a Janis VNF-100 cryostat. Appropriate long-pass filters with cutoff wavelengths a bit shorter than the excitation were inserted to the excitation beam to eliminate the influence of harmonic waves, whereas another a bit longer long-pass was sometimes put in the monitoring side to cut away the tail of the excitation beam.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03632.

Comparison of PL spectra intensity measured for same slit width (PDF)

## AUTHOR INFORMATION

### Corresponding Author

*E-mail: yoshidat@yz.yamagata-u.ac.jp* Phone: +81-238-26-3587.

### ORCID

Shuji Okada: 0000-0001-9519-6648

Philipp Stadler: 0000-0001-6459-5574

Oleg Dimitriev: 0000-0002-6848-6401

Tsukasa Yoshida: 0000-0003-0754-445X

### Author Contributions

K.U. and Y.T. prepared all the hybrid samples and carried out all measurements. S.O. and R.Y. synthesized DAST samples and provided general knowledge about organic NLO materials. L.S. and Y.S. gave technical advice for PL, PLE measurements, and data analysis. M.S.W. and M.F. provided general knowledge about exciton behavior in organic solid matters. P.S. discussed about dipole orientation of DAS in CuSCN matrix. O.D. discussed about possibilities of two-photon upconverted emission. T.Y. supervised the whole project and wrote the manuscript.

### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The present work was financially supported by Grant-in-Aid for Scientific Research (Kakenhi B, 18H02068) and Japan-Ukraine Bilateral Joint Research Project (organic/inorganic hybrid crystals for NIR to visible upconversion) from Japan Society for the Promotion of Science (JSPS) and the State Fund for Fundamental Research of Ukraine (project F80/3904).

## REFERENCES

1. Yoshida, T.; Tochimoto, M.; Schlettwein, D.; Wöhle, D.; Sugita, T.; Minoura, H. Self-assembly of zinc oxide thin films modified with tetrasulfonated metallophthalocyanines by one-step electrodeposition. *Chem. Mater.* 1999, 11, 2657–2667.

2. Yoshida, T.; Terada, K.; Schlettwein, D.; Oekermann, T.; Sugita, T.; Minoura, H. Electrochemical self-assembly of nanoporous ZnO/EosinY thin films and their sensitized photophotocatalytic performance. *Adv. Mater.* 2000, 12, 1214–1217.

3. Nonomura, K.; Yoshida, T.; Schlettwein, D.; Minoura, H. One-step electrochemical preparation of ZnO/Ru(dcbpy)(NCS) hybrid thin films and their photoelectronics properties. *Electrochim. Acta* 2003, 48, 3071–3078.

4. Yoshida, T.; Iwata, M.; Ando, H.; Oekermann, T.; Nonomura, K.; Schlettwein, D.; Wöhle, D.; Minoura, H. Improved photoelectrochemical performance of electrodeposited ZnO/EosinY hybrid thin films by dye re-adsorption. *Chem. Commun.* 2004, 400–401.

5. Yoshida, T.; Zhang, J.; Komatsu, D.; Sawatani, S.; Minoura, H.; Pauporté, T.; Lincot, D.; Oekermann, T.; Schlettwein, D.; Tada, H.; Wöhle, D.; Funabiki, K.; Matsu, M.; Miura, H.; Tanag, H. Electrodeposition of inorganic/organic hybrid thin films. *Adv. Funct. Mater.* 2009, 19, 17–43.

6. Yoshida, T.; Pauporté, T.; Lincot, D.; Oekermann, T.; Minoura, H. Cathodic electrodeposition of ZnO/EosinY hybrid thin films from oxygen-saturated aqueous solution of ZnCl2 and EosinY. *J. Electrochem. Soc.* 2003, 150, C608–C615.

7. Pauporté, T.; Yoshida, T.; Cortés, R.; Froment, M.; Lincot, D. Electrochemical growth of epipalaxial Eosin/ZnO hybrid films. *J. Phys. Chem. B* 2003, 107, 10077–10082.

8. Zhang, J.; Sun, L.; Icinose, K.; Funabiki, K.; Yoshida, T. Effect of anchoring groups on electrochemical self-assembly of ZnO/xanthene dye hybrid thin film. *Phys. Chem. Chem. Phys.* 2010, 12, 10494–10502.

9. Iwamoto, T.; Ogawa, Y.; Sun, L.; White, S. M.; Sariciftci, N. S.; Maneksi, K.; Sugita, T.; Yoshida, T.; et al. Electrodeposition of nanostructured CuSCN / Rhodamine B hybrid thin film and its dye-sensitized photocathodic property. *J. Phys. Chem. C* 2014, 118, 16581–16590.

10. Tsuda, Y.; Sun, H.; Sun, L.; Okada, S.; Masuhara, A.; Stadler, P.; Sariciftci, N. S.; White, S. M.; Yoshida, T. Electrochemical self-assembly of CuSCN-DAST hybrid thin films. *Monatsh. Chem.* 2017, 148, 845–854.

11. Tsuda, Y.; Uda, K.; Chiba, M.; Sun, H.; Sun, L.; White, M. S.; Masuhara, A.; Yoshida, T. Selective hybridization of organic dyes with CuSCN during its electrochemical growth. *Microsyst. Technol.* 2018, 24, 715–723.

12. O’Regan, B.; Grätzel, M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films. *Nature* 1991, 353, 737–740.

13. Oekermann, T.; Yoshida, T.; Tada, H.; Minoura, H. Color-sensitive photoconductivity of nanostructured ZnO/dye hybrid films prepared by one-step electrodeposition. *Thin Solid Films* 2006, S11–S12, 354–357.

14. Föhlinger, J.; Somnath, M.; Allison, B.; Edgar, M.; Sascha, O.; Leif, H. Self-quenching and slow hole injection may limit the efficiency in NIO-based dye-sensitized solar cells. *J. Phys. Chem. C* 2018, 122, 13902–13910.

15. Kim, M.; Park, S.; Jeong, J.; Shin, D.; Kim, J.; Ryu, S.-H.; Kim, K.-S.; Lee, H.; Yi, Y. Band-tail transport of CuSCN: Origin of hole extraction enhancement in organic photovoltaics. *J. Phys. Chem. Lett.* 2016, 7, 2856–2861.

16. Sun, L.; Icinose, K.; Sekiya, T.; Sugita, T.; Yoshida, T. Cathodic electrodeposition of p-CuSCN nanorod and its dye-sensitized photocathodic property. *Phys. Proced.* 2011, 14, 12–24.

17. Uda, K.; Tsuda, Y.; Okada, S.; Yamakado, R.; Sun, L.; Suzuki, Y.; White, M. S.; Furis, M.; Stadler, P.; Dimitriev, O. P.; Yoshida, T. Photoluminescent property of electrochemically self-assembled CuSCN/dye hybrid thin films. *ECS Trans.* 2019, 323–333.

18. Zhang, X.-C.; Ma, X.-F.; Jin, Y.; Lu, M.-T.; Boden, E. P.; Phelps, P. D.; Stewart, K. R.; Yakymyshyn, C. P. Terahertz optical rectification from a nonlinear organic crystal. *Appl. Phys. Lett.* 1992, 61, 3080–3082.

19. Kawase, K.; Mizuno, M.; Soma, S.; Takahashi, H.; Taniuchi, T.; Urata, Y.; Wada, S.; Tashiro, H.; Ito, H. Difference-frequency terahertz-wave generation in an organic crystal and its spectroscopic application. *J. Appl. Phys.* 2004, 95, 5984–5988.
(21) Kumar, K.; Rai, R. N.; Rai, S. B. One- and two-photon-pumped luminescence studies on DAST and UDAST organic dye molecules. Appl. Phys. B 2009, 96, 85−94.
(22) Lal, M.; Pakatchi, S.; He, G.-S.; Kim, K.-S.; Prasad, P. N. Dye-doped organogels: A new medium for two-photon pumped lasing and other optical applications. Chem. Mater. 1999, 11, 3012−3014.
(23) Okabe, K.; Sellk, Y.; Oekermann, T.; Yoshida, T. Cathodic electrodeposition of CuSCN thin films. Trans. Mater. Res. Soc. Jpn. 2008, 33, 1325−1328.
(24) Tsuda, Y.; Nakamura, T.; Uda, K.; Okada, S.; Sun, L.; Suzuki, Y.; Stadler, P.; Yoshida, T. Switching of dye loading mechanism in electrochemical self-assembly of CuSCN/DAS hybrid thin films. ECS Trans. 2019, 313, 313−322.
(25) Karthikeyan, C.; Hameed, A. S. H.; Nisha, J. S. A.; Ravi, G. Spectroscopic investigation on the efficient organic nonlinear crystals of pure and diethanolamine added DAST. Spectrochim. Acta, Part A 2013, 115, 667−674.
(26) O’Regan, B.; Schwartz, D. T. Electrodeposited nanocomposite n-p heterojunctions for solid-state dye-sensitized photovoltaics. Adv. Mater. 2000, 12, 1263−1267.
(27) Phillips, A. P. Condensation of aromatic aldehydes with 4-picoline methiodide. J. Org. Chem. 1949, 14, 302−305.
(28) Mineno, Y.; Matsuoka, T.; Ikeda, S.; Taniuchi, T.; Nakanishi, H.; Okada, S.; Adachi, H.; Yoshimura, M.; Moro, Y.; Sasaki, T. Single crystal preparation of DAST for terahertz-wave generation. Mol. Cryst. Liq. Cryst. 2007, 463, 337−343.