

Exciton transport and electron mobility of organized aggregates of cationic dye thiocyanates

Cite this: DOI: 10.1039/c2ra22538g

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Films of cationic dye thiocyanates adsorbed on copper based substrates form organized structures by a process of templated self-assembly. The growth process is initiated by strong S-bonding of thiocyanate ions to Cu sites, followed by repetitive and alternate bonding of dye cations and thiocyanate anions by electrostatic and dipolar forces. Rhodamine B thiocyanate and several other cationic dye thiocyanates solid films deposited this way exhibit J-aggregation behavior with large red-shifts in the absorption spectrum. Photoelectrochemical experiments with Rhodamine B thiocyanate deposited CuSCN cathodes indicated exciton diffusion lengths of order of 100 nm and space charge saturation current measurements suggested nearly three orders of magnitude enhancement of the electron mobility in the J-aggregated film. The photovoltaic properties of heterojunctions sandwiching J-aggregated dye films between n- and p-type semiconductor surfaces are investigated for potential application as solar cells and photon detectors.

Received 16th October 2012,
Accepted 18th December 2012

DOI: 10.1039/c2ra22538g

www.rsc.org/advances

1. Introduction

Light absorbed by organic solids creates Frenkel excitons diffusively transported until they decay *via* recombination or decompose into free carriers at an interface.^{1,2} Transport of excitons is greatly facilitated in organized molecular assemblies, notably J-aggregates where the transition dipole moments are strongly coupled.^{3–7} The properties of J-aggregates of organic molecules, especially those of dyes have been extensively investigated, both experimentally and theoretically, opening up novel optoelectronic device concepts. The possibilities of adopting J-aggregates in solar cells,^{8–10} photon detectors,¹¹ electroluminescent devices,^{12,13} excitonic transistors^{5,14} and switches,¹⁵ lasing systems and microcavity devices¹³ continue to attract much attention. Familiar photovoltaic and photoconductive photon detectors are based on inorganic semiconductors. Versatile low noise, low cost devices sensitive even to a single low energy photon may be devised adopting dyes and other organic compounds *via* molecular assembly-solid interface engineering.^{11,16,17}

Thin films of organized aggregates of small molecules, exhibiting fast exciton transport and mobility of one type of carrier (electron or hole) receive much attention as promising materials for development of excitonic solar cells and photon detectors.^{18–20} The basic operation mechanism of these devices is diffusion of photogenerated excitons, their decomposition at the boundary of another material with mobile

carriers of the opposite sign (hole or electron). Most J-aggregates have large exciton diffusion coefficients but low carrier mobilities while the H-aggregates exhibit the opposite behavior.²¹ The reason for low carrier mobility in J-aggregates seems to be the tendency for accumulation disorder in the film casting process than a fundamental constraint. Chromophore molecular assemblies with large exciton diffusion lengths and a high mobility for one type of carrier are desirable systems for many optoelectronic device applications.

In most studies, J-aggregated thin films of long range order are formed by Langmuir Blodgett technique, spin casting in a polymer matrix or *via* layer-by-layer deposition.^{22–25} In this note we describe a simple technique for deposition of highly organized J-aggregated thin films of cationic dye thiocyanates exhibiting large exciton diffusion lengths and enhanced electron mobilities on copper based substrates, CuSCN, CuI and Cu₂O. Mechanism involved is explained as strong S-bonding of the SCN[−] ions to the copper substrate and templated self-assembly of dye cations and thiocyanate anions to form a repetitive organized structure. Construction of a model solar cell of the configuration n-Cu₂O/J-aggregated Rhodamine B/p-CuI is described.

2. Experimental

Commercial (Aldrich) Rhodamine B in the chloride form (RhBCL) was converted to the thiocyanate (RhBSCN) by boiling the dye powder in a saturated aqueous solution of KSCN. The large excess of KSCN ensures that the reaction RhBCL + KSCN → RhBSCN + KCl proceeds in the forward direction. RhBSCN

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insoluble in cold aqueous KSCN, is separated, dissolved in ethanol and recrystallized. Recrystallized samples are subjected to the previous process a few times to purify the dye and eliminate all chloride. *p*-CuSCN was coated on copper plates ($1 \times 1.5 \text{ cm}^2$) electrolytically from an aqueous solution of KSCN containing propan-2-ol ($\sim 1 \text{ v\%}$).²⁶ *n*-Cu₂O was coated on copper plates ($1 \times 1.5 \text{ cm}^2$) by boiling the plates in a 10^{-4} M solution of CuSO₄ for several hours.²⁷ Fluorine doped conducting tin oxide (FTO) glass plates were coated with TiO₂ by spraying a solution of titanium isopropoxide in propan-2-ol and sintering at 450 °C. RhBSCN was deposited on *p*-CuSCN and *n*-Cu₂O coated copper plates by keeping the plates suspended in 0.05 M solution of RhBSCN containing 5% (volume) ethanol at 25 °C. A large volume of dye solution (100 mL) was kept magnetically stirred so that the effect of dilution due to dye adsorption is negligible. The amount of dye adsorbed was determined by extraction of the dye into ethanol and spectrophotometric estimation. As the linear dimension of the RhB molecule is $\sim 1.7 \text{ nm}$, 1 monolayer in $1 \text{ cm}^2 = 5 \times 10^{11}$ moles. The spectrophotometric detection limit of RhB $\sim 10^{-8} \text{ mol/litre}$, enables detection of ~ 1 monolayer in 1 cm^2 extracted into 1 cm^3 of ethanol. Optical microscopic examination of the film indicated that the film is uniform and aggregated dye grains embedded on the surface are absent.

The white light (tungsten filament lamp at 250 Wm^{-2}) photoresponse of the RhBSCN dye films deposited on different substrates were recorded by measuring the short-circuit photocurrent (I_{sc}) in photoelectrochemical cells (PECs) in 3-electrode configuration with a Pt counter-electrode and SCE standard, in an iodide/tri-iodide electrolyte.

Heterojunctions of the configuration *n*-Cu₂O/J-aggregated RhBSCN/*p*-CuI were fabricated as follows. A film of RhBSCN was deposited on *n*-Cu₂O coated copper plates by the method described above. Counter-electrode was prepared by coating $\sim 4 \mu\text{m}$ layer of CuI from a 0.3 M solution of acetonitrile containing $\sim 10^{-4} \text{ M}$ guanidinium thiocyanate acting as a CuI crystal growth inhibitor. The cell was formed by pressing and clamping the counter-electrode against the dye coated surface painted with CuI to establish contact. Heterojunctions *n*-TiO₂/J-aggregated RhBSCN/*p*-CuI were fabricated by growing a RhBSCN film on CuI deposited on FTO glass and pressing the TiO₂ coated FTO glass plate against the dye surface. The IV characteristics and the photocurrent action spectra were measured using a source meter and a monochromator set-up.

D.C electrical conductivities of solid RhBCl, RhBSCN were determined by two probe measurements using compacted pellets. The conductivity of the RhBSCN film deposited on copper based substrates was estimated by measuring resistance of the plates before and after deposition of the dye film. Electron mobilities of RhBCl, RhBSCN, RhBSCN films deposited on Cu substrates were estimated by measuring space charge saturated current using the Mott–Gurney equation.

3. Results and discussion

A peculiar phenomenon observed in adsorption of RhBSCN and many other thiocyanates of cationic dyes (XSCN) on copper based substrate (Cu, CuSCN, CuI, Cu₂O) plane surfaces is continuous increase of the thickness of the dye layer provided the dye solution is constantly homogenized maintaining a constant concentration. For a given solvent composition (vol% ethanol) and temperature, the film continues to grow if the dye concentration in the solution exceeds a critical value. The process of film growth can be understood as follows. Thiocyanate ions are strongly adsorbed on the surface *via* S-bonding to the Cu sites.^{28,29} Subsequently, the dye cation X⁺ bonds electrostatically bond to adsorbed SCN⁻ forming an organized monolayer of SCN⁻X⁺. The monolayer with X⁺ lying at the surface exposed to the solvent acts as a template, the dipolar forces attach SCN⁻ ion to SCN⁻X⁺ to form SCN⁻X⁺SCN⁻ and an electrostatic bond with X⁺ built two layers SCN⁻X⁺SCN⁻X⁺ and the processes continues indefinitely as represented schematically in Fig. 1. The initial strong bonding of SCN⁻ ions onto the Cu based surface followed by electrostatic bonding of the dye cation is the crucial condition that leads to formation of an organized J-aggregate of the dye, spread over a large area. In most familiar situations of J-aggregate formation of dye films on a surface, all the dye molecules are not identically oriented to form the first monolayer which acts as a template for the progressive growth of the dye film. The monolayer thickness of the film is estimated on basis of linear dimension of the dye molecule (RhBSCN $\sim 1.7 \text{ nm}$).

Variation of the short-circuit photocurrent (I_{sc}) of an RhBSCN coated *p*-CuSCN photocathode with the monolayer thickness of the dye film is shown in Fig. 2 as previously observed and published by the author (K.T) and his collaborators in their studies on dye sensitization, although the mechanism involved was not elaborated and explained.³⁰ According to Fig. 2, photocurrent sharply increases, reaching a maximum at a dye coverage corresponding to a monolayer, then declines and gradually increases reaching a much higher second maximum at dye coverage of approximately 46 monolayers, corresponding to a film thickness of $\sim 78 \text{ nm}$. On further increase of the film thickness, photocurrent decreases and beyond ~ 75 monolayers, it is too small for resolution against noise. The similar variation of I_{sc} with monolayer film thickness was seen in RhBSCN films deposited by the same procedure on CuI and Cu₂O surfaces but not on

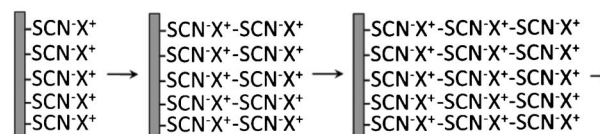


Fig. 1 Schematic representation indicating growth organized self-assembled thin film of the cationic dye XSCN (X⁺ = chromophore cation) on a copper based substrate.

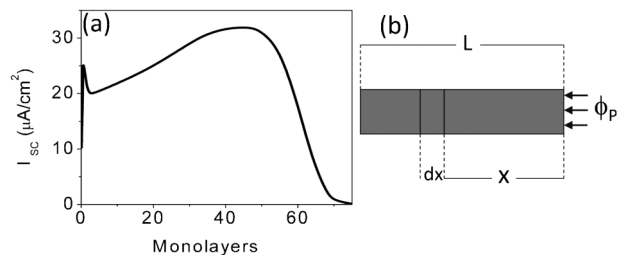


Fig. 2 (a) Variation of the short-circuit photocurrent (I_{sc}) of RhBSCN coated p -CuSCN photocathode in iodide/tri-iodide electrolyte (illumination 250 Wm^{-2} , Tungsten filament lamp). (b) Sketch explaining the dye film geometry used in derivation of eqn (1). Photon flux Φ_p is incident on dye film/electrolyte interface ($x = 0$), other interface ($x = L$) is CuSCN/dye.

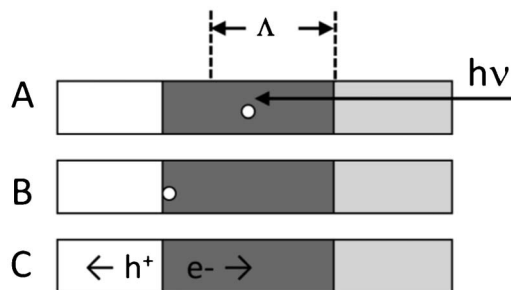


Fig. 3 Mechanism of photocurrent generation by in p -CuSCN (or p -CuI) photocathode deposited with RhBSCN J-aggregate. (A) Exciton creation by an absorbed photon, (B) exciton diffusing to the CuSCN/RhBSCN boundary, (C) hole and electron release to CuSCN and RhBSCN respectively (white rectangle – CuSCN, dark grey rectangle – RhBSCN, grey rectangle – aqueous electrolyte). The extent marked as Λ is the exciton diffusion length.

TiO₂. The absence of this behavior in RhBSCN deposited on TiO₂, clearly indicates that the template effect of SCN⁻ bonding to Cu based substrate has been the essential initial condition for the growth of an organized molecular assembly.

In familiar dye-sensitization, only the monolayer of molecules attached to the semiconductor surface inject carriers to a band. Generally, the excess dye molecules randomly agglomerated over the surface has a deleterious effect because of concentration quenching, while J-aggregation sometimes contribute favourably to the sensitized quantum efficiency^{31,32}. The unusual effect of enhanced sensitization by the significantly thick dye layer can be understood as follows: the absorption spectrum of an aqueous solution RhBSCN is peaked at $\sim 543 \text{ nm}$ and the peak of the photocurrent action spectrum of a RhBSCN monolayer coated p -CuSCN photocathode which corresponds to the first peak of Fig. 2, occurs at $\sim 554 \text{ nm}$. A red-shift of $\sim 11 \text{ nm}$ is a consequence of bonding the dye to the substrate surface. However, the peak of the action spectrum of the photocathode of the optimally thick film (46 monolayers) appears at $\sim 632 \text{ nm}$. The large red shift (78 nm) indicates J-aggregation and such structures have large exciton diffusion coefficients. The mean free path of light (λ) in the dye film calculated using the extinction coefficient of Rhodamine B ($1.06 \times 10^5 \text{ mol cm}^{-1}$) is $\sim 30 \text{ nm}$. At monolayer coverage, injection of holes from the excited dye molecules anchored to the CuSCN surface generates photocurrent. When the thickness of the dye film exceeds mean free path of light (λ), light cannot reach the CuSCN/dye interface and the photocurrent is generated by the following process (Fig. 3). Photons absorbed by the bulk of the dye create excitons which diffuse and decompose at the CuSCN/dye interface releasing holes to p -CuSCN and electrons to the dye. The positioning of HOMO of Rhodamine B and the valence band edge of CuSCN permits the above process. Rhodamine B being an electron mobile (n-type) material^{33,34} transports the electron to the electrolyte interface where it is accepted by tri-iodide.

The variation of photocurrent with the dye film thickness (Fig. 1) can be understood as follows. As dye coverage increases from zero, excited dye molecules anchored to surfaces, inject electrons increasing the photocurrent until a monolayer thickness is reached. When the next 1–2 mono-

layers begin to form, light cut-off from first monolayer reduces the photocurrent, as thickness further increase exciton process takes over until limited by the exciton diffusion length. A simple one-dimensional model presented below explains the variation of the excitonic photocurrent with the film thickness.

If Φ_p = photon flux incident on film surface (Fig. 2b), the flux at a distance x in the film is $\Phi_p \exp(-x/\lambda)$ (λ = mean free path of light) and light absorbed in an element of the film of thickness $dx = (\Phi_p/\lambda)\exp(-x/\lambda)dx$. In a one-dimensional model a half of excitons created in the element will travel forward and the other half in the backward direction and getting reflected at the front (dye/electrolyte) interface. Thus photocurrent dI generated from the excitons created in the element and incident on the dye/ p -CuSCN interface is,

$$dI = \frac{\Phi_p \Pi_p \Pi_D (1+r)}{2\lambda} e^{-x/\lambda} \left[e^{-(L-x)/\Lambda} + r e^{-(L+x)/\Lambda} \right] \quad (1)$$

Where, Λ = exciton diffusion length, Π_p = probability of exciton creation by light absorbed, Π_D = exciton decomposition probability at the CuSCN/dye interface, r = exciton reflection/reflection at the dye/electrolyte interface. Integrating (1), for $\Lambda > \lambda$.

$$I \approx \frac{\Phi_p \Pi_p \Pi_D}{2} e^{-L/\Lambda} [1 - e^{-L/\Lambda}] \quad (2)$$

The expression (2) is maximum, when $L = \Lambda \ln 2$ and the, giving $\Lambda = 112.6 \text{ nm}$. Thus the existence of a second maximum in the curve of Fig. 2 (a) is explained enabling estimation of the exciton diffusion length. As the photocurrent reaches a negligibly small value when the film is ~ 75 monolayers, corresponding to a film thickness of $\sim 128 \text{ nm}$, the value of Λ estimated from the model agrees reasonably well with the photocurrent measurement.

The D.C electrical conductivities and electron mobilities of RhCl, RhBSCN and a J-aggregated film of RhBSCN measured at 25°C are given in Table 1. Conductivity and electron mobility are nearly three orders of magnitude higher in the organized

Table 1 D.C electrical conductivities (σ) and electron mobilities (μ_e) of Rhodamine B chloride (RhBCL), Rhodamine B thiocyanate (RhBSCN), and a J-aggregated film of Rhodamine B thiocyanate grown over a CuSCN surface

	σ (S cm ⁻¹)	μ_e (cm ² V ⁻¹ S ⁻¹)
RhBCL	$\sim 10^{-8}$	$\sim 10^{-6}$
RhBSCN	3×10^{-7}	$\sim 10^{-6}$
RhBSCN (J-aggregate)	7×10^{-4}	8×10^{-2}

film. Molecular arrangement as in Fig. 1, greatly enhance the exciton diffusion length as well as the electron mobility.

The photocurrent action spectrum of the heterojunction n-Cu₂O/J-aggregated RhBSCN/*p*-CuI obtained by transmitting light through CuI is shown in Fig. 4. The narrow profile of the photocurrent action spectrum peaked at 632 nm and red-shifted 89 nm from the absorption peak of the dye solution, indicating J-aggregation. The curve C of Fig. 4 is action spectrum of n-Cu₂O/*p*-CuI. It is interesting to note that the photocurrent arising from Cu₂O band gap excitation (the broad profile peaked at 480 nm in the curve A of Fig. 4) is greatly enhanced in presence of the dye. This can be understood as suppression of surface recombination by the absorbed dye which passivates the Cu₂O surface. In dye-sensitized solar cells, the dye plays a key role in suppressing recombination *via* passivation of the surface.³⁵

Current–voltage characteristics of different heterojunctions examined are summarized in Table 2. The highest I_{sc} and η are obtained for the cell n-Cu₂O/J-aggregated RhBSCN/*p*-CuI with a RhBSCN film approximately ~ 29 monolayers thick. The monolayer thickness here is less than the optimum film thickness in the PECs with J-aggregated RhBSCN coated CuSCN photocathode. The reason for this behaviour appears to be the difference in the interfaces where exciton decomposition and reflection take place. However, quantitative analysis of the problem has not been successful. In the n-Cu₂O/J-aggregated RhBSCN/*p*-CuI system excitons decomposing at the RhBSCN/*p*-CuI interface contribute to the

Table 2 IV characteristics of different heterojunctions

Heterojunction	I_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF	η %
n-Cu ₂ O/ <i>p</i> -CuI	2.1	370	0.41	0.32
n-Cu ₂ O/RhBSCN (monolayer)/ <i>p</i> -CuI	3.2	390	0.50	0.62
n-Cu ₂ O/RhBSCN (J-aggregate)/ <i>p</i> -CuI	3.8	423	0.56	0.90
n-TiO ₂ /RhBSCN (J-aggregate)/ <i>p</i> -CuI	0.4	486	0.43	0.08

photocurrent injecting electrons to RhBSCN and holes *p*-CuI and excitons decomposing at n-Cu₂O/RhBSCN interface cannot contribute to the photocurrent as RhBSCN is n-type. The low V_{oc} of all the heterojunctions based on n-Cu₂O is due to interference of the Cu/n-Cu₂O contact as n-Cu₂O is deposited on metallic copper. The cell n-TiO₂/J-aggregated/RhBSCN/*p*-CuI delivers a higher V_{oc} , but the I_{sc} is low due to poor contact at the interface n-TiO₂/RhBSCN formed by pressing a TiO₂ coated FTO glass plate onto to the dye film.

Thiocyanates of Methyl Violet and several other cationic dyes demonstrated the same behavior in forming highly organized J-aggregated films on copper based substrates. A notable exception is Acridine Orange thiocyanate (ACSCN) deposited on CuSCN surface by the same procedure as RhBSCN. The absorption spectrum of an aqueous solution ($\sim 10^{-3}$ M) of ACSCN peaks at ~ 490 nm. However, the photocurrent of an ACSCN coated CuSCN photocathode reaches the maximum at 460 nm, indicating this dye forms H-aggregates when adsorbed on CuSCN. Again when the variation of the short-circuit photocurrent with monolayer thickness was examined, the optimum occurred at monolayer coverage, thereafter decreasing very rapidly with the increase of the monolayer thickness.³⁰ The variation of the short-circuit photocurrent with ACSCN film thickness (*i.e.* the equivalent of Fig. 1a for ACSCN) is shown in Fig. 5. Generally H-aggregates do not facilitate exciton transport and the cathode with a thick ACSCN film cannot deliver photocurrent *via* the exciton mechanism

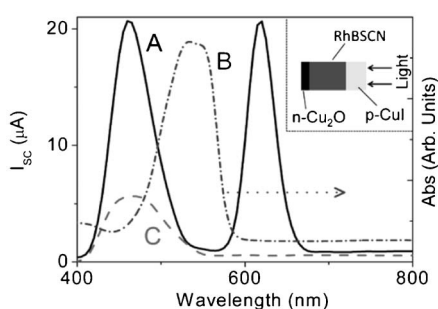


Fig. 4 (A) Photocurrent action spectrum of a n-Cu₂O/J-aggregated RhBSCN/*p*-CuI heterojunction shined with light as indicated in the inset (for clarity contacts to cell are not shown). The narrow peak to left in the curve A originate from light absorption by the dye and the broad peak is Cu₂O band gap excitation. (B) Absorption spectrum of aqueous RhBSCN. (C) Photocurrent action spectrum of n-Cu₂O/*p*-CuI.

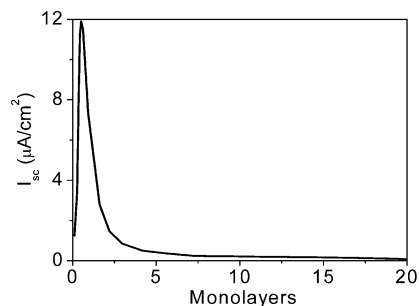


Fig. 5 Variation of the short-circuit photocurrent (I_{sc}) of ACSCN coated *p*-CuSCN photocathode in iodide/tri-iodide electrolyte (illumination 250 Wm⁻², Tungsten filament lamp).

4. Conclusion

The above study demonstrates that highly organized films of thiocyanates of cationic dyes can be deposited on copper based substrates by controlled absorption from a solution. The mechanism involved is strong S-bonding of SCN^- ion to Cu sites and repetitive attachment of dye cations and SCN^- ions alternatively to yield a thick film of organized structure. Thiocyanates of Rhodamine B, Methyl Violet and several other dyes deposited in this manner exhibited J-aggregation behaviour with widely red-shifted narrow absorption bands. Large exciton diffusion lengths of the order of 100 nm were evident from photoelectrochemical measurements and molecular organization has also enhanced the electron mobility. The purity of the dye and absence of imperfections in the molecular architecture are important to achieve large exciton diffusion lengths and high mobilities. These parameters may be further increased by improving the purification technique and carrying out the deposition at a lower temperature. Dyes used in this study are not the best, much higher efficiencies are expected when alternative dyes of high carrier mobilities are used. Efficient exciton and carrier transport depend on dye molecular structure and organization of molecules in the film, alternative dyes and optimized film deposition techniques are expected to yield higher photocurrent quantum efficiencies. Heterojunction structures constructed indicated the potential of dye films in solar cell application as both exciton diffusion length and electron mobility are enhanced by molecular organization. Probably the system is effectively one-dimensional and such structures could exhibit directional exciton transport.³⁶ The above strategy of growing organized molecular films may be extended to other organic cationic (anionic) dyes by appropriate choice anionic (cationic) moieties to render strong bonding to the surface of a selected material. Thiocyanate bonded to Cu sites readily act as an electron conduits. The problem establishing electronic coupling to the counter-electrode could be achieved by adhering polymer brush³⁷ terminated with a ligand that binds to moiety in the dye or by other similar strategies. Solar cells, NIR and IR detectors and sensors are potential applications. Chromophores absorbing in different regions of the spectrum could be organized by the same procedure to achieve panchromatic photoresponse. If the absorption and emission spectra of adjacent molecular layer overlaps, exciton transport through structure is possible *via* Förster energy transfer.

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