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Influence of Synthesized Thiourea Derivatives as a Prolific Additive with Tris(1,10-phenanthroline)cobalt(II/III)bis/tris(hexafluorophosphate)/ Hydroxypropyl Cellulose Gel Polymer Electrolytes on Dye-Sensitized Solar Cells

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**Graphical Abstract** 



Influence of Synthesized Thiourea Derivatives as a Prolific Additive with Tris(1,10-phenanthroline)cobalt(II/III)bis/tris(hexafluorophosphate)/ Hydroxypropyl Cellulose Gel Polymer Electrolytes on Dye-Sensitized Solar Cells

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#### Abstract

An exceptional approach of appending tris(1,10-phenanthroline)cobalt(II)/(III)bis/ tris(hexafluorophosphate) and synthesized tetramethyl benzidine-based thiourea derivatives as novel additives with hydroxypropyl cellulose are used to construct a gel polymer electrolyte for DSSC. The thiourea derivatives are synthesized using the cost-effective method. The synthesized derivatives are confirmed by <sup>1</sup>H, <sup>13</sup>C NMR and mass spectroscopy. The conductivity, surface and redox potential of thiourea derivatives doped Co<sup>2+/</sup>Co<sup>3+</sup> redox electrolytes are scrutinized by impedance spectra, FTIR, UV, XRD. A density functional theory method with full geometry optimization is used to elucidate the adsorption of the thiocarbamides on  $TiO_2$  (101) surface progressing with symmetrical electron donating/accepting groups. All the organic compounds display a negative shift on the TiO<sub>2</sub> Fermi level simultaneously by adsorption and rebutted as an escalated additive in stable Co(II/III)phen redox electrolyte of the dye-sensitized TiO<sub>2</sub> solar cell. This impulse effect influences the sorbate dipole moment component normal to TiO<sub>2</sub> surface plane; further, the stable redox mediator and hydroxypropyl cellulose deliver a good performance in a dye-

sensitized solar cell. The newly synthesized thiourea derivatives doped  $\text{Co}^{2+/}\text{Co}^{3+}$  with hydroxypropyl cellulose reports high solar to electric conversion, particularly **1,1'-(3,3',5,5'tetramethyl-[1,1'-biphenyl]-4,4'-diyl)bis(3-(3,4,5-trimethoxy phenyl)thiourea) (additive-6)** doped redox electrolyte shows an outstanding efficiency ( $\eta$ ) of **9.1%** under the sunlight irradiation of about **70 mW/cm**<sup>2</sup>.

#### **Keywords**

Tris(1,10-phenanthroline)cobalt(II)/(III)bis/tris(hexafluorophosphate) redox couple, Hydroxylpropyl cellulose, Gel polymer electrolyte, Thiourea, TiO<sub>2</sub> additive, DFT, Dyesensitized solar cells

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#### **1. Introduction**

Global energy consumption is expanding rapidly in recent times by the depletion of natural sources. To eradicate this concern, much focus has been attributed to the adoption of renewable energy resources, typically solar energy [1-3]. Conversion of solar energy into the electricity and for the design of photovoltaic gadgets will make an articulate role for the amending of energy consumption and a quick fix for a long-term energy crisis. Gratzel and O'Regan developed such a device with low-cost and high efficiency ( $\eta$ ) i.e., 11% via simple fabrication in 1991, the so-called dye-sensitized solar cell (DSSC) [4]. The DSSC is build of working electrode as TiO<sub>2</sub> coated with Ru based dye, electrolyte with iodide/iodine as a redox couple and counter electrode as platinum [5-7]. Among all, the electrolyte takes the athletic

portrayal in intensifying efficiency proportion in DSSC. Different types of electrolytes are habituated so far on our planet. A broader aspect is taken up by the liquid electrolyte [8] but there are some disadvantages like leakage, poor chemical and physical stability. To deracinate from such issues, surrogate admittance is undoubtedly by the gel electrolyte [9]. Many research works have been implemented so far using such electrolyte for attaining good efficiencies and improvement of shelf time storage in DSSC. It has more superior assets like non-volatile nature, high stability, high ionic conductivity responsive to novel packing, little self-discharge and low vapour pressure [10,11]. Thereupon for the preparation of gel polymer electrolyte, several studies have been done by earning higher efficiencies using cellulose [12]. Recently, Hydroxypropyl cellulose was used in gel polymer electrolyte to gain a maximum efficiency of 5.79% [13]. HPC possess extraordinary physical, chemical, stability property, and are highly preferable by their biodegradable property, so this favours the choice rather than using general polymers like polyethylene glycol, polyvinylidene fluoride, polycaprolactone, etc [9].

In the reign of semiconductor TiO<sub>2</sub>, out of three phases, the anatase crystal is the more photoactive. The anatase (101) surface tempted more attention by its lower surface energy compared to (100) and (001) surface and it is scrutinized to adsorb small molecule on its surface which is thermodynamically more stable [14]. These are prominent and evident by its regularly perceived tetragonal bipyramidal growth habit. The interfaces amidst rutile and anatase are further considered to increase charge carrier separation and facilitate the photocatalytic activity. As a result, biphasic titanium dioxide is considered to contain enhanced functionality as a photocatalyst [15].

Towards redox couple,  $\Gamma/I_3^-$  is the classic oxidized/reduced for many years by grating iodide salts and iodine. The cations of the added iodide salts and the concentration of iodide

with triiodide in the redox couple hike the photocurrent-voltage tone [16,17]. Nevertheless, this redox pair has achieved valuable efficiencies, but it has many consequences like the large difference between their energy level with HOMO of the sensitizer results in shrink of  $V_{OC}$ , slow electron self-exchange kinetics, high vapour pressure which give up the balance module of DSSC. To heal up the disadvantages, various eminent scientists introduced the application of bromine, nitroxide radicals and organic redox mediators[18]. But they limit the efficiency of the solar cell due to the slow recombination of electrons in the cathodic part to the oxidized redox specimens. Succeeding, transition-metal-based redox couples proved to be more efficient and stable. Among which cobalt-based redox couple showed a colossal improvement in the efficiency of a solar cell [19-23]. Mastermind in DSSC i.e., Gratzel and his co-workers achieved 12.3% (ŋ) by using zinc porphyrin sensitizer and cobalt-based oxidized/reduced duo [24].

In the convention, additives and co-additives such as 4-tert-butylpyridine (TBP), guanidinium thiocyanate (GuSCN) etc, are utilized to improve the efficiency to a certain extent by shifting the potential to negative in TiO<sub>2</sub> [25-29]. Sarcastically the conjugated hetero-organic dopants pave the way for the architectural flow of electrons from them to the polymer and redox pair which helps in accumulating prosperous ionic conductivity in the entire DSSC set up. Recently, thioureas have gained importance as additives [30-33] in a polymer matrix for improving the efficiency in DSSC and reached a whopping efficiency of 7.17% [34]. Thus, we focussed our efforts on synthesizing thiourea derivatives using electron rich tetramethyl benzidine at the core with thiourea at the periphery as a whole for synthesizing thiourea derivatives with cost-effective methods. The synthesized thioureas posses a very strong adsorption on the TiO<sub>2</sub> surface and shifts the band edge to negative potential rapidly. Further, blending these additives with the hydroxypropyl cellulose, ethylene carbonate, propylene carbonate, as plasticizers and the redox pair i.e., tris(1,10-

phenanthroline)cobalt(II)/(III) bis/tris(hexafluorophosphate) boosted up the photophysical and photovoltaic properties of the electrolyte. The influence of the additives in the GPE has been discussed by its electrochemical, photovoltaic, diffraction, calorimetric, and vibrational characterization. And the synthesized thiourea derivatives are subjected to DFT calculations to evaluate the adsorption energy of the molecules towards the TiO<sub>2</sub>.

#### 2. Experimental Section

#### 2.1 Chemicals and Reagents

Hydroxypropyl cellulose Mw~370000, ethylene carbonate, 2-amino-6-methylpyridine, thiophosgene, propylene carbonate, methanol (anhydrous) and all the isothiocyanates were purchased from Aldrich and the 3,3',5,5'-tetramethylbenzidine, triethylamine, sodium bicarbonate, dichloromethane was purchased from AVRA synthesis Pvt. Ltd. Fluorine-doped tin oxide coated glass slide L x W x D 100mm x 100mm x 2.3mm surface resistivity ~7  $\Omega$ /sq and Titanium(IV)oxide, anatase nanopowder, <25 nm particle size, 99.7% trace metals basis were purchased from Aldrich.

#### 2.2 Synthesis of Organic additives

The thiourea additives are synthesized using a very mild and cost-effective method. The general scheme is depicted in **Figure 1**. The corresponding isothiocyanate was stirred with 3,3',5,5'-tetramethylbenzidine in anhydrous methanol at room temperature for 2-3 days to obtain the product as a white precipitate which was then filtered, washed with methanol and dried under vacuum.

2.2.1 Synthesis of 1,1'-(3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'-diyl)bis(3-(4-butylphenyl)thiourea)-Additive-1

1-butyl-4-isothiocyanatobenzene 0.875g (2.2 equiv.) with 0.5g (1 equiv.) 3,3',5,5'tetramethylbenzidine was stirred in 40ml of anhydrous methanol at room temperature for 2-3 days. The product obtained was a white precipitate which was then filtered, washed with methanol and dried under vacuum to obtain **1,1'-(3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'diyl)bis(3-(4-butylphenyl)thiourea)** as a white solid with 75% yield. The corresponding scheme is depicted in **Fig. S1.** <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz) δ (ppm): 9.84 (br s, 2H, 2NH), 8.90 (br s, 2H, 2NH), 7.41–7.36 (m, 8H), 7.10 (s, 4H), 2.57-2.54 (m, 4H), 2.29 (s, 12H), 1.58-1.52 (m, 4H), 1.33-1.29 (m, 4H), 0.92-0.89 (m, 6H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 125 MHz) δ (ppm): 180.75, 139.15, 137.29, 129.09, 128.99, 128.93, 126.57, 126.45, 123.97, 34.81, 33.67, 22.21, 18.77, 14.28; HRMS (ESI): calcd. For **C<sub>38</sub>H<sub>46</sub>N<sub>4</sub>S<sub>2</sub>** [M+H]<sup>+</sup> 623.3164 found 623.3238. (**See Supp. data S1, S2, S3, S4**)

# 2.2.2 Synthesis of 1,1'-(3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'-diyl)bis(3-(4-chlorophenyl)thiourea)- Additive-2

1-chloro-4-isothiocyanatobenzene 0.776g (2.2 equiv.) with 0.5g (1 equiv.) 3,3',5,5'tetramethylbenzidine was stirred in 40 ml of anhydrous methanol at room temperature for 2-3
days. The product obtained was a white precipitate which was then filtered, washed with
methanol and dried under vacuum to obtain **1,1'-(3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'- diyl)bis(3-(4-chlorophenyl)thiourea)** as a white solid 75% yield. The corresponding scheme
is depicted in **Fig. S5**. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz)  $\delta$  (ppm): 10.03 (br s, 2H, 2NH), 9.08
(br s, 2H, 2NH), 7.58-7.57 (d, 4H), 7.42-7.41 (d, 4H), 7.40 (s, 4H), 2.28 (s, 12H); <sup>13</sup>C NMR
(DMSO-d<sub>6</sub>, 125 MHz)  $\delta$  (ppm): 185.60, 143.67, 143.54, 141.98, 133.71, 132.97, 132.89,
131.20, 129.98, 23.49; HRMS (ESI): calcd. For **C<sub>30</sub>H<sub>28</sub>Cl<sub>2</sub>N<sub>4</sub>S<sub>2</sub> [M+H]<sup>+</sup> 579.1132 found
579.1206. (See Supp. data S5, S6, S7, S8)** 

## 2.2.3 Synthesis of 1,1'-(3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'-diyl)bis(3-(4-methoxyphenyl)thiourea) Additive-3

1-isothiocyanato-4-methoxybenzene 0.756g (2.2 equiv.) with 0.5g (1 equiv.) 3,3',5,5'tetramethylbenzidine was stirred in 40 ml of anhydrous methanol at room temperature for 2-3 days. The product obtained was a white precipitate which was then filtered, washed with methanol and dried under vacuum to obtain **1,1'-(3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'diyl)bis(3-(4-methoxyphenyl)thiourea)** as a white solid with 78% yield. The corresponding scheme is depicted in **Fig. S9**. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz)  $\delta$  (ppm): 9.71 (br s, 2H, 2NH), 8.76 (br s, 2H, 2NH), 7.37-7.37 (m, 4H), 7.32-7.31 (m, 4H), 6.92 (s, 4H), 3.74 (s, 6H), 2.26 (s, 12H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 125 MHz)  $\delta$  (ppm): 180.99, 157.15, 137.34, 137.27, 126.71, 126.47, 126.43, 126.32, 114.49, 55.72, 18.75; HRMS (ESI): calcd. For **C<sub>32</sub>H<sub>34</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup> 571.2123 found 571.2198. (See Supp. data S9, S10, S11, S12)** 

# 2.2.4 Synthesis of 1,1'-(3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'-diyl)bis(3-(naphthalen-1-yl)thiourea)-Additive-4

1-isothiocyanatonaphthalene 0.847g (2.2 equiv.) with 0.5g (1 equiv.) 3,3',5,5'tetramethylbenzidine was stirred in 40 ml of anhydrous methanol at room temperature for 2-3 days. The product obtained was a white precipitate which was then filtered, washed with methanol and dried under vacuum to obtain **1,1'-(3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'diyl)bis(3-(naphthalen-1-yl)thiourea)** as a white solid with 70% yield. The corresponding scheme is depicted in **Fig. S13**. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz)  $\delta$  (ppm): 9.95 (br s, 2H, 2NH), 8.70 (br s, 2H, 2NH), 8.07-8.04 (m, 2H), 8.00-7.98 (m, 2H), 7.91-7.88 (m, 2H), 7.64-7.61 (m, 2H), 7.57-7.56 (m, 4H), 7.36-7.33 (m, 2H), 7.21 (s, 2H), 7.13 (s, 2H), 2.13 (s, 12H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 125 MHz)  $\delta$  (ppm): 181.81, 143.89, 139.07, 136.39, 135.45, 134.14, 130.31, 128.17, 127.21, 126.27, 125.95, 125.67, 124.58, 122.98, 120.93, 18.48; HRMS (ESI): calcd. For C<sub>38</sub>H<sub>34</sub>N<sub>4</sub>S<sub>2</sub> [M+H]<sup>+</sup> 611.2225 found 611.2297. (See Supp. data S13, S14, S15, S16)

# 2.2.5 Synthesis of 1,1'-(3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'-diyl)bis(3-(4-nitrophenyl)thiourea)-Additive-5

1-isothiocyanato-4-nitrobenzene 0.824g (2.2 equiv.) with 0.5g (1 equiv.) 3,3',5,5'tetramethylbenzidine was stirred in 40 ml of anhydrous methanol at room temperature for 2-3 days. The product obtained was a white precipitate which was then filtered, washed with methanol and dried under vacuum to obtain 1,1'-(3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'diyl)bis(3-(4-nitrophenyl)thiourea) as a white solid with 68% yield. The corresponding scheme is depicted in Fig. S17. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz)  $\delta$  (ppm): 10.09 (br s, 2H, 2NH), 9.52 (br s, 2H, 2NH), 8.24–8.22 (m, 4H), 7.98–7.96 (m, 4H), 7.43 (s, 4H), 2.30(s, 12H); <sup>13</sup>C NMR (DMSO-d6, 125 MHz)  $\delta$  (ppm): 180.13, 146.42, 142.03, 138.56, 136.69, 136.02, 126.12, 124.56, 120.88, 120.80, 18.22; HRMS (ESI): calcd. For C<sub>30</sub>H<sub>28</sub>N<sub>6</sub>O<sub>4</sub>S<sub>2</sub> [M+H]<sup>+</sup> 601.1613 found 601.1687. (See Supp. data S17, S18, S19, S20)

# 2.2.6 Synthesis of 1,1'-(3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'-diyl)bis(3-(3,4,5-trimethoxyphenyl)thiourea)-Additive-6

5-isothiocyanato-1,2,3-trimethoxybenzene 1.03g (2.2 equiv.) with 0.5g (1 equiv.) 3,3',5,5'-tetramethylbenzidine was stirred in 40 ml of anhydrous methanol at room temperature for 2-3 days. The product obtained was a white precipitate which was then filtered, washed with methanol and dried under vacuum to obtain 1,1'-(3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'-diyl)bis(3-(3,4,5-trimethoxyphenyl)thiourea) as a white solid with 75% yield. The corresponding scheme is depicted in Fig. S21. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500

MHz) δ (ppm): 9.86 (br s, 2H, 2NH), 8.93 (brs, 2H, 2NH), 7.38 (s,4H), 6.81 (s, 4H), 3.77(s, 18H), 2.23 (s, 12H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 125 MHz) δ (ppm): 179.83, 152.78, 136.75, 136.31, 134.79, 134.57, 125.93, 121.19, 101.23, 60.03, 55.77, 18.33; HRMS (ESI): calcd. For C<sub>36</sub>H<sub>42</sub>N<sub>4</sub>O<sub>6</sub>S<sub>2</sub> [M+H]<sup>+</sup> 691.2546 found 691.2622. (See Supp. Data S21, S22, S23, S24)

# 2.2.7 Synthesis of 1,1'-(3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'-diyl)bis(3-(6-methylpyridin-2-yl)thiourea)-Additive-7

2-isothiocyanato-6-methylpyridine was synthesized by treating 2-amino-6-methyl pyridine (1 equiv.) with thiophosgene (1.1 equiv.) in a mixture of  $CH_2Cl_2$  and saturated aqueous solution of NaHCO<sub>3</sub> (1:1 v/v) at 0°C for 2 h. Then, the organic layer was separated and evaporated to give the product as a pale yellow solid with 92% yield. Generally, the isothiocyanates vary instability so it is used in the next step without further purification.

2-isothiocyanato-6-methylpyridine 0.687g (2.2 equiv.) with 0.5g (1 equiv.) 3,3',5,5'tetramethylbenzidine was stirred in 40 ml of methanol at room temperature for 2-3 days. The product obtained was a white precipitate which was then filtered, washed with methanol and dried under vacuum to obtain **1,1'-(3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'-diyl)bis(3-(6methylpyridin-2-yl)thiourea)** with 85% yield. The corresponding scheme is depicted in **Fig. S25**. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz)  $\delta$  (ppm): 13.13 (br s, 2H, 2NH), 10.88 (br s, 2H, 2NH), 7.74-7.70(t, 2H), 7.44 (s, 4H), 7.07-7.05(d, 2H), 6.96-6.94(d, 2H), 2.42 (s, 6H), 2.29 (s, 12H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 125 MHz)  $\delta$  (ppm): 179.62, 154.71, 153.27, 139.51, 138.41, 136.31, 135.75, 126.13, 117.22, 109.57, 23.59, 18.45; HRMS (ESI): calcd. For **C<sub>30</sub>H<sub>32</sub>N<sub>6</sub>S<sub>2</sub> [M+H]<sup>+</sup>** 541.2130 found 541.2206. **(See Supp. data S25, S26, S27, S28)** 

#### 2.3 Preparation of thiourea doped gel polymer electrolytes (GPE)

The GPE's were prepared by blending hydroxylpropyl cellulose (0.300g), Co(II)phen (0.030g), Co(III)phen (0.030g), propylene carbonate and ethylene carbonate (1:1 ratio) (1 g) and synthesized organic additive (0.010g) at 100°C until homogenous mixture was obtained. The mixture was cooled to ambient temperature to obtain the corresponding GPE. The undoped GPE were tested for DSSC applications and the obtained data was compared with the doped GPE electrolytes system blended with organic additives 1-7. The GPE images are represented in **Figure 2**.

#### 2.4 Fabrication of DSSC

The DSSC using GPE were fabricated using the nanocrystalline TiO<sub>2</sub> cast on fluorinated tin oxide (FTO) conducting glass by the reported procedure [35]. The TiO<sub>2</sub> coated methanol electrodes are drenched for 24 hours in solution containing a ditetrabutylammonium cis bis (isothiocyanato) bis (2,2'bipyridyl4,4'dicarboxylato) ruthenium(II) N719 dye and it formed the working electrode of the DSSC. The active area of DSSC was 1 cm<sup>2</sup> (1cm x 1cm). The GPE with thiourea derivative was placed between the N719 dye coated TiO<sub>2</sub> (working-electrode) and platinum (counter-electrode). Decisively, DSSC (sandwich type) was fabricated by holding both the electrodes together with the use of alligator clips. Further, all the measurements were performed at room temperature.

#### **2.5 Computational Details and Methods**

#### 2.5.1. Gas Phase Optimization

The thiourea derivatives of tetramethyl benzidine containing different functional groups were studied. The experimentally synthesized organic compounds were analyzed using the computational investigation to study the efficiency of the molecules for dye-sensitized solar cell applications. The geometry optimizations (i.e. gas phase) at the ground

state were done using density functional theory (DFT) approach, Becke's three-parameter hybrid exchange functional and Lee-Yang-Parr correlation functional (B3LYP) [36]. Earlier studies have shown that the DFT-B3LYP method is more suitable to predict the electronic properties of the large size organic molecules [37,38] and the same with 6-311++G\*\* basis set was employed for all molecule optimization [39,40]. All electronic structure calculations were performed using *GAUSSIAN 16* and *GaussView 6.0* and Chemcraft software's were used for visualization [41].

Initial coordinates were built from GaussView 6.0 and gas phase optimization followed by frequency analysis was done at B3LYP/6-31G\* method. Then we used these coordinates for the high-level electronic structure calculation. The energy gap ( $E_g$ ) between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are calculated from optimized geometries. This analysis can help to understand the electronic transition between HOMO-LUMO and the calculated value can be used to study the effect of functional groups present in the side chain. The lower the  $E_g$  easy to transfer the electron from HOMO to LUMO for DSSC application [42].

#### 2.5.2. Organic Molecules at TiO<sub>2</sub> Surface

Optimized geometries of organic molecules were used to study the adsorption behaviour of different orientation of these molecules at TiO<sub>2</sub> anatase (101) surface. Since the titania normally used is foremost anatase. Thus the molecules were placed over the surface particularly and were freely optimized at TiO<sub>2</sub> surface to predict the different properties such as adsorption energy ( $E_{ad}$ ) and shortest interacting distances (hydrogen bonding, vdWs,  $\pi$ - $\pi$  stacking to the surface). In addition, we have also calculated Fermi energies for TiO<sub>2</sub> after the adsorption of additives. All the geometry optimizations were done using CP2K/Quickstep code [43]. All DFT calculations are based on hybrid GPW (Gaussian plane wave) [44] and

PBE (Perdew- Burke- Enzerhof) [45] exchange-correlation functional. A plane wave cut off of 600 Ry was used. Grimme D3 [46,47] method is employed for dispersion corrections to study the effect of dispersion. For atoms Ti and O we have used DZVP (Double- Zeta Valance Polarized) [48] and for all other atoms, we used TZVP (Triple-Zeta Valance Polarized) [49] basis sets. After optimization, the adsorption energies and Fermi energies were calculated using the same method.

The adsorption energies, shortest N-H····O hydrogen bond distances, the shortest distance between the aromatic ring and TiO<sub>2</sub> surface further Fermi energies were analyzed and are given in Table 2. Adsorption energies are calculated using Equation 1,

### $\mathbf{E}_{ad} = - \{ \mathbf{E}_{(TE)} - [\mathbf{E}_{(Additive)} + \mathbf{E}_{(Surf)}] \} \text{Equation (1)}$

Here  $E_{ad}$  denotes the adsorption energy of organic molecule on TiO<sub>2</sub> surface,  $E_{TE}$  stands for the total energy of the complex system,  $E_{Additive}$  and  $E_{surf}$  are the energy of individual organic molecule and TiO<sub>2</sub> surface, respectively.

#### 2.6 Characterization

The undoped and doped thiourea derivative GPE's with  $Co^{2+/}Co^{3+}$  are subjected to electrical, vibrational, absorption, diffraction and photovoltaic characterization. The FTIR spectrum was recorded using FTIR, SHIMADZU IR TRACER with the frequency range of 400-4000cm<sup>-1</sup>. The absorption band due to Co(II/III)phen with GPE and organic additives in DMF were measured by using UV-Vis spectrophotometer ANALYTIK JENA, SPECORD 210 plus. Further, conductivity was evaluated by the impedance analysis using FTO glass slide as electrodes and rubber O-ring as separator under Biologic SP-300. The X-ray diffraction patterns were recorded using PANalytical x'pert powder X-ray diffractometer using CuK $\alpha$  radiation. The NETZSCH DSC 204 F1 Phoenix instrument was used to analyze

the differential scanning calorimetry (DSC) plot and understand the thermal response of the GPE. The current-voltage curves were measured under BAS100A electrochemical analyzer. Under standard filter conditions by utilizing 150 W tungsten halogen lamp (OSRAM, Germany) as light source under 1.5 AM illumination. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using BRUKER 500 MHz. HR Mass spectra were recorded using LC/MS, 6230B Time of Flight (TOF), Agilent technologies.

#### **3. Results and Discussion**

#### **3.1.1 Ionic Conductivity**

The examination of the resistance of the samples was done by potentiostatic electrochemical impedance spectroscopy technique in the specific nyquist plot, at room temperature. The scan range was fixed from 500 kHz to 300 mHz and it was observed in single sine mode to set Ewe to E of GPE as 0.800V. The resistivity was obtained well enough from the intercept on the real axis at a higher frequency. It is shown in **Fig.S29** (See Supp. data). Further, the conductivity was measured from the resistance since both are inversely related.

The formula utilized is as follows:

$$\boldsymbol{\sigma} = \boldsymbol{t} / (\boldsymbol{R}_{b}\boldsymbol{A})$$

Where,

t is the thickness of the gel polymer electrolyte,

A is the area of the sample's surface,

 $R_b$  is the bulk resistance of the material

**Figure 3** provides the electrical conductivity of the undoped GPE and seven additives with GPE and cobalt redox couple in this study were calculated to be of  $5.04 \times 10^{-5} \text{ Scm}^{-1}$ ,  $1.36 \times 10^{-4} \text{ Scm}^{-1}$ ,  $1.18 \times 10^{-4} \text{ Scm}^{-1}$ ,  $1.37 \times 10^{-4} \text{ Scm}^{-1}$ ,  $1.05 \times 10^{-4} \text{ Scm}^{-1}$ ,  $1.02 \times 10^{-4} \text{ Scm}^{-1}$ ,  $1.43 \times 10^{-4} \text{ Scm}^{-1}$ ,  $1.16 \times 10^{-4} \text{ Scm}^{-1}$ . It is noted that the **1,1'-(3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'-diyl)bis(3-(3,4,5-trimethoxyphenyl)thiourea)** (additive 6) reached the highest ionic conductivity of **1.43 x 10^{-4} Scm**^{-1} which is higher than the undoped GPE by almost one degree of magnitude which clearly imply that due to the effective redox couple pairing with the polymer and the additives. The ionic conductivity increased upon the addition of the additives with the HPC under ambient temperature. Hence conductivity gets strongly boosted by the presence of a well-conjugated system with thiocarbamide linkage group and electron donating groups present in the organic additive which exalt the mobility and elasticity of ions. Even though by the addition of the remaining additives, the conductivity exalted due to the presence of highly electron donating groups followed by electron withdrawing groups when compared with the undoped GPE.

#### **3.1.2 Electrochemical Impedance Spectroscopy**

EIS spectroscopy is the predominant technique to analyse the interfacial and electrical properties of the electrolytes. The nyquistic plot and equivalent circuit of the polymer electrolytes are used to scrutinize the chemical capacitance and charge transfer resistance which isobtained using the fitting from the EIS spectra. The Impedance spectra of DSCs are measured in dark at a potential of 0.8 mV close to  $V_{oc}$ . Generally EIS of DSCs contains three distinct arcs, initial and the light independent high frequency arc corresponds to the electrolyte and the Pt interface, the second arc and the light-dependent mid frequency arc corresponds to the electrolyte interface with TiO<sub>2</sub> and the dye which is one of the vital characteristics to improve the DSCs performance which has direct effect on  $V_{oc}$  of the cells.

The final low-frequency arc corresponds to the Warburg resistance. The EIS obtained using DSC setup is shown in Figure 4. The equivalent circuit used for interpreting impedance is shown in Figure 5. Where Rs is the series resistance and C1, R1 is the capacitance and charge transfer resistance in the Pt-electrolyte interface. C2 and R2 is the capacitance and charge transfer resistance in the TiO<sub>2</sub> and electrolyte interface, W is the Warburg resistance. The R<sub>CT</sub> value tends to increase on implementing additives to the pristine polymer electrolytes indicating the reduction of interfacial recombination in the electrolytes and improving the  $V_{oc}$  of the cells rapidly.  $R_{CT}$  and  $C_{\mu}$  were also obtained at different bias potential to evaluate the electrochemical properties of the electrolytes [50]. It is clearly shown in Figure 6 and 7. The electron density of states of the TiO<sub>2</sub> can be determined from C<sub>u</sub> which is an indirect measure of the Fermi level and was found to be increasing with the applied potential. The additives added gave an upward displacement in the  $TiO_2$  CB by adsorption which was proved by the displacement in  $C_{\mu}$  values. The displacement in the CB was attributed by the electron-donating and withdrawing groups present in the molecules. As discussed earlier in computational studies the molecule possessing more electron-donating groups like additive 6 was adsorbed more on the  $\rm TiO_2$  which resulted in better FF,  $V_{\rm oc}$  and  $J_{sc}$ of the cells. The shift in chemical capacitance and conduction band of the semiconductor will reduce the electron diffusion rate and the electron injection efficiency which has a direct effect on the  $J_{SC}$ . The upward shift in the TiO<sub>2</sub> can also be due to the usage of cobalt redox shuttle rather than potassium or sodium iodide salts which are well known for downward displacement in TiO<sub>2</sub> CB [51,52]. The J<sub>sc</sub> of the cell was also improved by the addition of additives due to the increase in the ionic conductivity and mobility in the HPC polymer matrix. And thus the impact of additives on the solar cell parameters was clearly proved by the means of theoretical and experimental studies.

#### **3.2 Differential Scanning Calorimetry and Diffraction data**

DSC characterization of the GPE's was measured and the range was fixed between -  $40^{\circ}$ C to  $300^{\circ}$ C. The heating rate is 10 K/min. The thermogram shows decomposition temperature (T<sub>dc</sub>) of 186°C respectively for undoped GPE. Rather than it shows the blunt peak at 126°C and 60°C. As seen in **Figure 8** (Additive 1-7) the decomposition temperature varied 185, 189, 186, 200, 182, 181 and 183°C due to the incorporation of the organic additives, cellulose and cobalt redox electrolyte. Even it attains the new decomposition temperature in a distinct range like 144, 143, 142, 157, 171, 142 and 138°C.

X-ray diffraction peaks were examined for  $\text{Co}^{2+/}\text{Co}^{3+}$  GPE doped with newly synthesized thiourea derivatives and undoped GPE. It is depicted in **Figure 9**. It clearly shows that electrolytes are more amorphous in nature due to its gel consistency. As seen in **Figure 9** (Additive 1-7), it shows a broader peak at 30° which confirms that the additive 1-7 well interacts with GPE and increases the electrolyte ability and conductivity. In addition, all the eight GPE the crystalline peak is not observed even after the summation of organic additives. It ensures that the organic additives are well jumbled with the Co(II/III)phen and cellulose. This result also holds good with conductivity studies.

#### 3.3 Vibrational and Absorption spectra

The vibration spectrum of the cellulose, Co(II/II) redox with/without organic additives were analyzed by the attenuated total reflectance infrared (ATR-IR) spectrum at room temperature. The FTIR spectrum scanning range is from 400 to 4000cm<sup>-1</sup>. It is shown in **Figure 10**. The broad transmission band at 3600-3200cm<sup>-1</sup> is due to the stretching of the hydroxyl groups in HPC can be remarkably distinguished. It can be seen that the peak intensity and the peak shape were clearly different for undoped GPE apart from the addition of organic additives with HPC and these differences were induced by the different organic compounds i.e., thioureas. The presence of hydrogen-bond could be inferred from the peak

shape and intensity of the absorption band of the hydroxyl stretching vibrations in the FTIR spectrum. C=S stretching is observed at  $1200 \text{cm}^{-1}$  and the C=O from PC and EC were at  $1650 \text{cm}^{-1}$ . The broadband in the undoped HPC is maximum at  $3471 \text{ cm}^{-1}$ , was assigned to stretching vibrations of the -OH groups and pyranose unit. The bands at  $2930 \text{cm}^{-1}$  and  $2863 \text{cm}^{-1}$  are due to CH<sub>2</sub> and CH stretching vibration. Interestingly the peak at  $2930 \text{ cm}^{-1}$  get sharpened and the peaks at  $1799 \text{cm}^{-1}$  get shortened these changes clearly shows that organic additive gets infused well with Co redox pair and HPC. The absorption band at  $1503 \text{ cm}^{-1}$  is due to C=C stretching vibration and at  $1073 \text{ cm}^{-1}$  is due to C-O-C stretching vibration which is the most important part of cellulose. The peaks at  $1090 \text{ cm}^{-1}$  get broadened in most of the additives. In **Figure 10**, the vibrations for additive 1-7 with HPC between 640 to  $880 \text{cm}^{-1}$  region gets shrunk this shows that there is a good linkage of the synthesized organic dopant with hydroxypropyl cellulose, Co(II) and Co(III).

UV-Vis absorption of the GPE's was analyzed for all the eight samples in DMF at room temperature. It is explicated in the **Fig.S30** (See Supp. data). The absorption band at 268 is due to undoped GPE. Organic additives which are added to the undoped GPE got the absorption peak as follows: 266, 273, 272, 267 and 269 for additive 1 to 4; 268, 310, 381 for additive-5; 269 for additive-6; 266 and 300 is due to additive-7. The different absorption peaks were observed for different functional group attached elucidated clearly the uniform blending of the polymer with the additives. These results clearly imply that the synthesized organic additives are based on transitions of n or  $\pi$  electrons to the  $\pi^*$  excited state. Since the experimentally obtained absorption peaks match with the general aromatic  $\pi$ - $\pi^*$  and n- $\pi^*$ transition wavelength i.e., 200-700 nm. And it even shows worthwhile that there is no impact of an unsaturated group in the molecules. It is further analyzed through DFT studies with HOMO LUMO calculations typically for organic additives at gas phase.

#### 3.4 Computational details of band edge shift and its adsorption process

Table 1 provides the HOMO-LUMO gap (Eg) for all additives calculated from DFT method. It was found that experimental efficiency order data is in very good agreement with our calculated Eg values. In order to check the charge transfer phenomena in organic additives, we have studied frontier molecular orbital (FMO) analysis. **Fig. S31 (See Supp. data)** shows the different FMOs of additives considered for the composite materials. This clearly reveals that there is a long-range charge transfer through aromatic  $\pi$ - $\pi$ \* and n- $\pi$ \* transition. It can be seen that HOMO orbital always localized in the –S atom irrespective of the electron donating/withdrawing group in the side chain.

The FMO analysis is done using the same functional and basis set (B3LYP/6-311++G\*\*). Orbitals such as HOMO-1, HOMO, LUMO, LUMO+1, LUMO+2 were analyzed and electron density pictures were taken. From this, we get a clear picture of how the charge transfer takes place in different orbitals. From the Eg (Table 1) it was found that additive 5(-nitro) has the lowest energy gap (Eg) and hence will show a better charge transferability when compared with other additives. The order of magnitude of Eg values obtained from DFT methods is close agreement with experimental efficiency values. The calculated Eg order with respect to the functional group present in the side chain is – pyridine>–chloro>–butyl~>trimethoxy>–methoxy>–naphthyl>–nitro. Here we found that the role of functional groups in organic linker plays a vital role in the charge transfer through  $\pi$ clouds.

From Table 2, it is clear that the adsorption is more for electron donating groups and is decreasing for electron withdrawing groups. Adsorption of linker on  $TiO_2$  surface reveals that the electron releasing groups were strongly adsorbed when compared with electron withdrawing groups. It is found that  $-(OMe)_3$ , -butyl and -OMe groups are strongly adsorbed

and the calculated E<sub>ad</sub> is varied from 418.0 to 450.0 kcal/mol. Other additives have less E<sub>ad</sub>, particularly additive 5 (nitro) have very less E<sub>ad</sub> (i.e.275 kcal/mol). Additive 2 (chloro) have moderate binding with  $TiO_2$  surface. It can be seen from the optimized geometries of the complex that there are various types of non-covalent interactions present (such as hydrogen bonding, vdWs,  $\pi$ - $\pi$  stacking to the surface). These interacting distances are shown in **Figure** 11. The shortest H-bond distances between -NH group of additives and O of TiO<sub>2</sub> surface is shown in **Figure 11** and also the shortest distance is given in Table 2. This H-bond shows the effective interaction between the molecule and the TiO<sub>2</sub> surface. Also, we found that aromatic ring perfectly adsorbed on the surface, this is a favour for the complex stability. From the optimization steps, it is clear that the aromatic ring and -NH group orient itself towards the  $TiO_2$  surface irrespective of the functional group present in the side chain. It helps the additives to have a better adsorption on the surface. But the adsorption energies vary based on the functional groups present as discussed above. Also, the Fermi energies are explained in Table 2. Additive 3 and additive 6 has lesser Fermi energies compared to other additives and thus an easy charge transfer after adsorption on the surface. It is important to note that these two additives are strongly bound to the surface. From the above-mentioned results, it is clear that strongly adsorbed additive have more charge transfer.

#### 3.5 Photovoltaic effects

The current-voltage (I-V) curve of DSSC fabricated cell using GPE's is measured by its photovoltaic achievement at 1.5 AM under sunlight irradiation of about 70mW/cm<sup>2</sup> and it is illustrated in Table 3. The corresponding I-V curve was depicted in **Figure 12**. The illustration of gel polymer electrolytes was carried away without any special sealing to value its concordance. The short circuit current ( $J_{sc}$  (mA)), open-circuit voltage ( $V_{oc}$  (mV)), fill factor (ff) and energy conversion ( $\eta$ ) data attained were listed in Table 3 clearly. Out of all

GPE's the one with more electron donating groups (OMe)<sub>3</sub> i.e., additive 6 resulted with the highest efficiency of about 9.1%. Since the overall order of efficiency for all the remaining seven GPE's goes on from electron donor groups ends up with an electron withdra4wing group. **Figure 13** denotes the error bar for the efficiency which shows the reproducibility of GPE's efficiency for all the samples. It visibly implies that all the GPE's are stable well enough and retain its liable reproducibility for several hours. The utilized cobalt redox pair can attain a  $V_{oc}$  of above 1V more than  $\Gamma/I_3^-$  and promoted the efficiency by its more positive redox potential. And furthermore, the importance of less light absorption and less disruptive nature on the metal surfaces by cobalt redox couples in DSSCs can improve the efficiency [53,54].

#### 4. Conclusion

In brief, the results revealed that symmetrical thioureas with more electron donating groups are the most stable and possess high adsorption energy towards the TiO<sub>2</sub>. These additives shifted Fermi level of TiO<sub>2</sub> (101) anatase. In addition, Cobalt redox pair escalated the efficiency by its predominating properties. HPC played the vital role in the electrolyte for boosting up the performance of the DSC by its excellent ionic mobility and conductivity. The results exemplified that the additives with more electron donating groups i.e., additive 6 (OMe)<sub>3</sub> seems to the best. It is believed that this opens the way to synthesize a variety of thioureas with numerous donating groups and engage DSSC with a wise band shift values on working electrode leads to high open-circuit voltage, low photocurrent density and even higher efficiencies in GPE. Thioureas usually have very high thermal, chemical stability and can be utilized as a robust additive. Thus employing these additives gave a very good efficiency in the range of **5.59-9.1%**.

#### **Conflicts of interest**

There are no conflicts to declare.

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### Appendix A. Supplementary Data

Supplementary data containing Schemes, <sup>1</sup>H NMR, <sup>13</sup>C NMR, HR MASS and UV data related to this article can be found at doi.

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## Table 1:

Organic	HOMO-LUMO gap			
molecule	E <sub>g</sub> (eV)			
Additive-1	4.13			
Additive-2	4.21			
Additive-3	4.08			
Additive-4	3.85			
Additive-5	3.40			
Additive-6	4.13			
Additive-7	4.31			

### Table 2:

Organic	E <sub>ad</sub>	N-H····O	TiO <sub>2</sub>	Fermi
Molecule	(kcal/mol)	Distance(Å)	surface····πDistance(Å)	energy(eV)
Additive-1	417.86	1.77	3.35	-5.00
Additive-2	314.84	1.78	3.07	-3.77
Additive-3	448.54	1.67	3.32	-3.51
Additive-4	284.46	1.80	3.24	-3.77
Additive-5	274.84	1.76	3.51	-4.09
Additive-6	450.07	2.04	3.43	-3.54
Additive-7	286.85	1.68	2.86	-3.75

### Table 3:

System	Current	Voltage	Fill factor	Efficiency
	(mA)	(mV)	( <b>ff</b> )	(%)
НРС	7	790	0.50	3.95
Additive-1	11.7	881	0.52	7.65
Additive-2	10.4	875	0.52	6.76
Additive-3	11.9	885	0.53	7.97
Additive-4	9.4	870	0.51	5.95
Additive-5	8.9	863	0.51	5.59
Additive-6	13.4	895	0.53	9.10
Additive-7	9.9	872	0.53	6.53

Figure 2



Note: HPC-Stands for hydroxypropyl cellulose with  $Co^{2+}/Co^{3+}$  redox; A-stands for additive with HPC and  $Co^{2+}/Co^{3+}$  redox



Note: HPC-Stands for hydroxypropyl cellulose with  $Co^{2+}/Co^{3+}$  redox; A-stands for additive with HPC and  $Co^{2+}/Co^{3+}$  redox























Additive-7







Note: HPC-Stands for hydroxypropyl cellulose with  $Co^{2+}/Co^{3+}$  redox; A-stands for additive with HPC and  $Co^{2+}/Co^{3+}$  redox

#### "Research Highlights"

- ✓ Introduction of coherent hydroxypropyl cellulose for gel polymer electrolyte.
- ✓ Simple and cost-effective synthesis of thiourea.
- ✓ Thioureas behave as a systematic additive on  $TiO_2(101)$ .
- ✓ Gel polymer electrolyte facilitates enhanced electrical conductivity.
- ✓ The gel polymer electrolyte with thiourea based DSSC shows good performance and high photovoltaic conversion 9.1 %.