Dipolar Imidazoanthraquinoe Derivatives and Their Application in Solid State Devices

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Abstract – Imidazoanthraquinone based mixtures (AQ01-AQ07) were orchestrated and described. Mixtures AQ01 and AQ02 were chosen for additional investigations. Photo physical properties in different solvents recommended the polar idea of the ground state for AQ01 and AQ02. Fluorescence extinguishing tries different things with the normally utilized electron contributor poly-3-hexylthiophene found out the capability of these particles as electron acceptor for applications in sun based cell gadgets. Thickness practical hypothesis (DFT) gave knowledge on the dipolar nature, H-holding, and π - π collaboration in various kinds of supramolecular gatherings of AQ01 and AQ02. Computations anticipated that the π - π cooperation through antiparallel direction and Bonding with the OH•••OH association is vivaciously preferred in AQ01. Morphological investigations on thermally dissipated meager movies showed nano-gatherings like interconnected wires in AQ01 while blossom like irregular totals in AQ02. Charge transport properties of these atoms were assessed for AQ01/AQ02 and their mixes with Poly(3-hexylthiophene-2,5-diyl) (P3HT). Opening portability in the AQ01-based gadget was observed to be of request of 10–4 cm 2/V s. High opening versatility got for AQ01 relates well with the positive morphology saw in the slim film. Our outcomes show that the dipolar atom AQ01 can possibly be utilized as a non-fullerene based electron acceptor in BHJ sun powered cell gadgets.

Key Words – Dipolar Imidazoanthraquinoe Derivatives

INTRODUCTION

Natural polar particles have been read for their applications in different arising fields, for example, mass hetero intersection (BHJ) sunlight based cells, non-direct optics and so on Natural atoms are generally considered as possible contender for photovoltaic gadgets on account of minimal expense, ecological cordial, simple handling, enormous region and adaptable gadgets. The working of a natural photovoltaic (OPV) gadget can be perceived in three sections: absorption and exaction arrangement charge partition and transportation and assortment of electrons and openings at separate terminals. Natural particles with wide absorption in noticeable and close to infrared districts are liked as dynamic light retaining materials for OPV gadgets. Upon light absorption, atom gets invigorated by advancing one electron from its HOMO to LUMO leaving behind an opening in the ground state, accordingly framing an exaction pair. This exaction pair is then isolated to get distinctive charge transporters. The so shaped charge transporters move to individual anodes where they are gathered. The exactions shaped may recombine which diminishes the gadget proficiency. Subsequently, productive charge partition and high transporter versatility are envious for predominant gadget execution. Proficient charge transporter transport is needed from one particle to other without being caught or dispersed. The portability of charge transporter is impacted by different factors like atomic plan, pollutants, temperature, pressure, electric field, thickness, size of particles, sub-atomic weight and so on Other than them, physical properties of materials utilized as dynamic layers in strong state gadgets like dielectric steady, morphology in slim film and so on are additionally assume a significant part for powerful transporter portability's. For a long time, natural dipolar particles were not considered as possible materials for strong state gadgets because of their low transporter versatility's. Borsenberger and Bassler revealed that dipolar gatherings make an irregular electrostatic potential in nebulous strong state materials which brings about bigger lively issue that diminishes the charge bouncing. Accordingly, dipolar atoms and even particles with dipolar practical gatherings were not considered as possible voltaic materials for natural photo and semiconducting materials. Later on, the use of dipolar atom having high opening mobilities in OPV (Organic Photo Voltaic) was accounted for. The dipole second being a vector amount relies upon the course of the dipoles in a polar atom. It was accounted for by Wurthener et al. that in mass the dipole snapshot of individual atom doesn't assume a huge part alone. The stacking or sub-atomic course of action in strong condition of particles prompting development of dimers might bring about the

reduction of generally speaking viable dipole second. Accordingly, ideal morphology is vital for the net dipole second and improved transporter mobilities. A couple of natural atoms having high dipole second were accounted for. Particles I and II both have solid electron pushing and pulling gatherings while in every one of the six electron pulling out fluorine iotas are in a facial game plan. Position of electron giving or electron pulling out bunches is capable somewhat for inconsistent conveyance of electron thickness. In compound, the impact of high dipole second is seen on better charge partition.

The distinctions in morphology might emerge because of the various techniques utilized in gadget manufacture. Kitchen et al. announced that in P3HT with expansion in more _face on'stacking may move the most noteworthy involved atomic orbital (HOMO) energy level which straightforwardly influences the OPV open-circuit voltage (VOC). Jung et al. likewise detailed the impact of stacking on the opening versatility and execution of gadgets. They further detailed tuning of morphology with strengthening at various temperatures. Negi et al. as of late considered the components which modify the morphology and presumed that turning rate, giver acceptor (D-A) blending proportion, dissolvable decision and so forth are likewise answerable for the adjustment of morphology and along these lines the gadget proficiency They further detailed tuning of morphology with toughening at various temperatures. Negi et al. as of late contemplated the variables which modify the morphology and inferred that turning rate, benefactor acceptor (D-A) blending proportion, dissolvable decision and so on are additionally answerable for the adjustment of morphology and hence the gadget productivity. Wang et al. read structure-property connections for bis-diketopyrrolopyrrole and detailed the impact of morphology in natural photovoltaics. Thus, comprehend the variables which influence the morphology, pressing construction, stacking and charge transport property in slim film gadgets. Morphology of natural materials can be adjusted by picking the reasonable center atom and setting the substituent bunches which instigate H-holding stacking or other bury sub-atomic collaborations.

P3HT and PCBM particles are generally utilized as contributor and acceptor atoms individually in natural sunlight based cells. Tremendous measure of work has been done to track down the reasonable substitute for contributor atom. Notwithstanding, for acceptor particle less work has been done and investigated. PCBM and other fullerene subsidiaries are exorbitant and they have restricted steadiness. Likewise, it is hard to deliver fullerene subordinates at mechanical scale. As of late, PCBM has been snubbed by non-fullerene particles as an acceptor in mass hetero intersection sunlight based cells as practical other option. All things considered, there is a need to observe to be better option as the accessible option doesn't show preferred proficiency over the fullerene subordinates.

Materials having contributor and acceptor moieties are known as benefactor acceptor particle. Properties of based materials can be changed by setting the substituent bunches on benefactor and acceptor or by fluctuating the of contributor acceptor moiety. The development of self-get together is good in frameworks by non-holding cooperation's. The nonholding communications are both intra sub-atomic just as intermolecular. The arrangements of such get together blessing improvement in the charge transporter portability's. Worthier et al. exhibited the capability of dipolar particles in strong state gadgets, inferable from which in this section, we mean to plan and blend little dipolar atoms to examine their slight film, morphological and gadget properties.

Photo physical studies

Absorption spectra of molecules AQ01-AQ07 were recorded in dichloromethane and data are summarized in. A broad band above 400 nm for * transition. An intense high energy π -compounds AQ01-AQ07 is attributed to n * transition. The extinction coefficient and broad π - π peak at ~300 nm is assigned for nature of higher wavelength absorption (400-500 nm) band show the features of charge transfer.

Absorption and emission studies of AQ01 and AQ02

AQ01 and AQ02 were chosen for additional photo physical, morphological and gadget contemplates. AQ01 has solid electron giving gathering on the benefactor unit when contrasted with AQ02. These two mixtures were chosen to study and analyze the impact of solid electron giving gathering in D-A frameworks. The absorption spectra of mixtures AQ01, AQ02 were likewise recorded in acetonitrile and meager strong movies. Slight strong movies were ready by turn covering just as by warm dissipation of AQ01, AQ02 on guartz plate. A shower chromic shift of 40 nm for AQ01 and 25 nm for AQ02 in flimsv strong movies were seen when contrasted with their spectra in acetonitrile. This shift proposed that there is collection in slim movies because of solid between atomic attractions. The emission maxima, in acetonitrile, for AQ01 and AQ02 were seen at 561 and 567 nm, separately. The photo physical properties for both AQ01 and AQ02 are summed up.

solvatochromic studies

The electronic properties of benefactor acceptor atoms are relied upon to be influenced by the extremity of the solvents; consequently, it was important to read the solvatochromism for intensifies AQ01 and AQ02. The absorption and emission properties of AQ01 and AQ02 were concentrated in various solvents of changing extremity. A tiny change in the absorption spectra of AQ01 and AQ02 was seen with various extremity solvents. The emission spectra for both AQ01 and AQ02 were

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recorded by intriguing the atoms close to the absorption maxima for example ~ 480 and 420 nm separately. The emission maxima of AQ01 showed a shift of ~ 80 nm in various extremity solvents while for AQ02 the shift was ~ 50 nm. A minimal change in the absorption maxima and huge change in the emission maxima propose that the low power top for both AQ01 and AQ02 is related with charge move in the particles. The degree and indication of solvatochromism additionally rely on the capacity of a compound to frame H-holding either by tolerating hydrogen bonds or giving H-bonds.

Lippert-mataga equation studies

The Lippert-Mataga (L-M) conditions were utilized to consider the adjustment of conduct of electronic properties of mixtures AQ01 and AQ02 with change in extremity of solvents. The L-M conditions give the proportion of the dipole snapshot of mixtures in left state to its ground state.

Lippert-Mataga conditions (1) and (2) are a guess which is utilized to ascertain the proportion of dipole minutes in ground state and left state.

$$(v_n - v_l) = 2(\mu_n - \mu_g)^2 / hca^3 [\{(n-1)/(2n+1) - (n^2 - 1)/(2n^2 + 1)\}] + K$$
 (1)

$$(v_s+v_l) = -2(\mu_c^2 - \mu_g^2)/hca^3[\{(c-1)/(2c+1)+(n^2-1)/(2n^2+1)\}].+K^3$$
 (2)

V_a and V_f are the absorption and emission wave number (in cm⁻¹), μ_e and μ_g are the exited state and ground state dipole moments respectively, ϵ is dielectric constant and *n* is the refractive index of the solvents. h is the Plank's constant, c is the speed of light and a is the Onsager cavity radius. K and K' are constants. The ratio of the dipole moments are calculated from the slopes of plot of (V_a-V_f) against the polarity parameters F1 and (V_a+V_f) against the polarity parameter F2 where $F1=\{(\epsilon-1)/(2\epsilon+1)-(n^2-1)/(2n^2+1)\}$ and $F2=\{(\epsilon-1)/(2\epsilon+1)+(n^2-1)/(2n^2+1)\}$ The wavenumbers for absorption and emission maxima are shown in for AQ01 and AQ02 respectively.

The Lippert-Mataga conditions think about particles as a point dipole and a persistent mode of uniform dipole second. It likewise ignores the polarizability of the fluorophores. The cooperations like H-holding among fluorophores and dissolvable atoms or development of charge move state digress the L-M condition from its overall hypothesis. furthermore, shows the plot of L-M conditions for intensifies AQ01 and AQ02. L-M condition couldn't fit straightly, henceforth, proposing the chance of solid charge move state or H-holding or both. From Figures, it very well may be seen obviously that the focuses are dispersed and a line plot couldn't be gotten for both the mixtures AQ01 and AQ02.

Fluorescence quenching studies

In mass hetero-intersection (BHJ) sun based cell, one of the significant boundaries is the exchange of charge from the benefactor to acceptor particles. The particle assimilates light and electron and opening sets are shaped, which might be lost in the event that they recombine. Consequently, for a particle to go about as a superior acceptor the charge move ought to be quick from contributor to acceptor to keep away from the deficiency of excitons through recombination. To really take a look at the capability of mixtures AQ01 and AQ02 as an electron acceptor, atomic fluorescence extinguishing test was done with P3HT (Poly(3hexylthiophene-2,5-diyl)) as electron benefactor and the outcomes were contrasted and P3HT:PCBM framework. PCBM (Phenyl-C61-butyric corrosive methyl ester) is a fullerene based acceptor which is generally utilized in electronic gadgets. A mix of AQ01 or AQ02 and PCBM in (w/w) proportion in chloroform was ready and twist cited on quartz plate at 2000 rpm for 40 seconds to get a uniform strong film. Likewise, slight film of P3HT:PCBM was additionally turn projected. The fluorescence was recorded for P3HT:PCBM, P3HT:AQ01 and P3HT:AQ02 mixes and the spectra are displayed in. All the emission spectra were recorded by thrilling the absorption band of P3HT at 514 nm and the cut width was kept steady as 5 nm. It very well may be seen from the that the emission spectra of P3HT in slick film is extinguished by every one of the three mixes. The mixes of AQ01 and AQ02 with P3HT showed extinguishing similar to P3HT:PCBM mix. The extinguishing demonstrates quick electron move from P3HT to AQ01 and AQ02 which shows that these mixtures can possibly be utilized as electron acceptor in BHJ sun powered cells.

Electrochemical studies

To get the knowledge on the red bull conduct of mixtures AQ01 and AQ02 and to assess the HOMO-LUMO energy levels, cyclic voltammetric studies were done in acetonitrile. The cyclic voltammograms were performed with polished carbon as working terminal, platinum wire as counter anode, Ag/AgCI a source of perspective cathode and as tetrabutylammonium hexafluorophosphate as supporting electrolyte. Compound AQ01/AQ02 was broken up in acetonitrile with supporting electrolyte and ferrocene was added as a kind of perspective for oxidation potential. Both AQ01 and AQ02 showed an irreversible oxidation top at ~1.9 V which is alloted to oxidation of imidazole moiety. The two mixtures AQ01 and AQ02 showed two irreversible decrease tops at ~1.0 and 1.7 V, which are allocated to carbonyl of anthraquinone.55 The HOMO and LUMO energy levels were assessed utilizing oxidation and first decrease possibilities (versus Fc/Fc+) and are observed to be - 6.6 eV and - 3.7 eV for compound AQ01 and - 6.6 and - 3.6 eV for compound AQ02, individually. The reference EHOMO for Fc/Fc+ was taken as - 5.1 eV. The photo physical and electrochemical properties of mixtures AQ01 and AQ02 are summed up beneath in.

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Hydrogen bonding interaction

We recognized the hydrogen holding collaboration between (I) the anthraquinone C-O and C-H of both the monomers, addressed as OH-OH just as (ii) the anthraquinone C-O and C-H from the substituent's interceded by imidazole NH bond, addressed as OH-NH. The hydrogen bond length for both the mixtures was unique. For compound AQ01, the OH-OH and OH-NH bond length was observed to be Å, separately, while for compound AQ02, the OH-OH and OH-NH security length was observed to be . Å. separately. The individual hydrogen bond energies for both the mixtures were likewise determined. For compound AQ01 the OH-OH and OH-NH bond energy were determined to be - 6.03 and - 3.96 kcal/mol, separately. For compound AQ02 these energies were determined to be - 5.42 and - 6.09 kcal/mol, separately. It was tracked down that the OH-OH energy for compound AQ02 was marginally lower by 0.6 kcal when contrasted with compound AQ02, though the hydrogen holding energy for OH-NH was higher by 2 kcal/mol in compound AQ02 when contrasted with compound AQ01. Hypothetical DFT computations information for hydrogen holding in AQ01 and AQ02 are summed up in.

Morphological studies

Good morphology of dynamic natural layers in gadgets assumes a urgent part as it impacts the transporter versatility's and the gadget execution. As examined before, stacking influences the open-circuit voltage (V(OC)) and the opening versatility in sunlight based cells. It has been seen that the development of nanocongregations in organics have prompted the better gadget performance.Formation of interconnected pathways structures an organization for productive charge transportation to the terminals where they are gathered. Little natural atoms total or self-gather in dainty movies to frame the nanostructures. Not very many reports are accessible to anticipate the morphology and control of self-conglomeration in dainty movies Both mixtures AQ01 and AQ02 have diverse utilitarian gatherings subbed on the center anthraquinone atom. These practical gatherings are relied upon to change the properties of the two atoms AQ01 and AQ02. The intermolecular holding in both these particles is additionally expected to vary because of the distinction in the electronic idea of the two atoms. The equivalent has been anticipated by the DFT computations. AQ01 and AQ02 both blessing intermolecular hydrogen holding between the NH bunch and the CO gathering. Consequently, it becomes important to contemplate the morphology of flimsy movies of atoms AQ01 and AQ02. The slight movies were concentrated by X-Ray Diffraction (XRD), which showed the shapeless idea of the particles. The microstructures of the slim strong movies of AQ01 and AQ02 were considered utilizing field emission filtering electron microscopy (FE-SEM). Slim movies were made by keeping the mixtures over Si substrates through warm vanishing under vacuum or by means of twist covering. The slight movies utilized for SEM

pictures have a thickness of 30 and 60 nm. The SEM pictures of thermally vanished film shows distinctive morphology when contrasted with that of twist covered. As displayed in Figure the SEM pictures of AQ01 show the development of a few m long nanowires. For a 30 nm dainty film of compound AQ01, the length of m. We accept that the intermolecular hydrogen nanowires was observed to communication work with the nanowire be arrangement in particle AQ01. We D bonding and have additionally seen that with expanding the thickness of the movies the thickness of these nanowires likewise increments and true to form, results in the intercalated or interconnected pathways. Then again, the dainty film of compound AQ02 show the development of little bloom like designs whose size increments with expanding the thickness of the flimsy film. The size of the bloom like nanostructures for a 30 nm thick film of AQ02 was observed to be almost 500 nm. These bloom like constructions were observed to be conveyed all around the surface yet didn't shape the interconnected pathways with expanding thickness as seen in AQ01. In this manner, morphological investigations propose that the difference in substituent's causes adjustment in surface morphology. Change in surface morphology can impact the charge transport properties in natural electronic gadgets.

Device fabrication and carrier mobility determination

In natural photovoltaic (OPV) gadgets, the charge transporters produced during the activity should ship effectively to arrive at the individual anodes. The exaction dispersion length is in couple of nanometers along these lines, the versatility turns into an essential boundary for the presentation of the gadget. As talked about before, there are reports which recommend that the natural atoms with high dipole minutes can't be utilized in natural photovoltaic gadgets as they have low charge transporter versatility's. Here, we report that intensifies AQ01 and AQ02 have high dipole minutes as they gather in enemy of equal style proposed by estimations. Subsequently, it becomes DFT important to examine the charge transporter versatility's of AQ01 and AQ02 in strong state gadgets. The transporter versatility's were dictated by utilizing the space charge restricted current (SCLC) model where the current thickness of the gadget is relative to the voltage. Likewise, in this model, the conduction of charge transporters for example openings and electrons in the gadget are restricted to the space charge impacts and not by the infusion of transporters at the contacts. In low fields, transporter versatility electric the is determined by Mott-Gurney law as displayed underneath.

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$$\sqrt{J} = \frac{3}{2\sqrt{2}} \frac{\sqrt{\varepsilon\mu}}{L^{\frac{3}{2}}} V$$

is the permittivity of the dynamic natural layer, Here, J is the current thickness, V is voltage, is the transporter mobility L is the thickness of the dynamic layer in the deviceµ and is the transporter versatility.

Hole only and electron only devices

In SCLC model, it is accepted that there is just a single types of charge transporter for example either opening or electron. Consequently, opening and electron versatility's are determined independently with this technique utilizing the electron just and opening just gadgets. The opening just gadgets were manufactured utilizing the gadget math: ITO/PEDOT:PSS/AQ01 or AQ02 mixed with P3HT/MoO3/Ag . The mix was made with the electron contributor P3HT Electron just gadgets were created utilizing gadget math as ITO/ZnO/AQ01 or AQ02 mixed with P3HT/LiF/AI

The versatility's were assessed by plotting \sqrt{J} versus V (voltage V = Vapp - Vbi, where Vapp is the applied voltage and Vbi is the counterbalanced voltage) at low electric fields and fitting it with the Mott-Gurney law. The opening versatility's were observed to be a few significant degree higher than their electron portability's intended for AQ01 while for AQ02 the opening and electron mobilities were of same request. For AQ01, the most elevated opening portability was observed to be 1.23 x 10-4 cm 2/Vs though electron versatility was observed to be 2.8 x 10-7 cm 2/Vs. The opening and electron mobilities for AQ02 were observed to be in the scope of 9.6 x 10-6 to 1.4 x 10- -6 cm 2/Vs. As the portability was estimated on thermally dissipated movies which had projecting components, there are chances of vulnerability in getting the thickness of the movies which lead to the blunder bar in the assessment of transporter versatility. In the space-charge restricted locale, versatility is identified with the thickness of the movies (see Mott-Gurney law). The physical beginning of this crisscross has been generally credited to the presence of extraneous snare states. A more explicit justification the confuse can be perceived through definite quantum mechanical estimations. It was shown that even with an enormous bungle between the opening and electron portability, such materials can be utilized in OPV showing high short out current thickness (Jsc) values. In this manner, AQ01 can be utilized as a productive electron acceptor in modified kind sun based cell gadgets expecting high shortcircuits current thickness esteems.

he high opening versatility of AQ01 when contrasted with AQ02 can be clarified based on morphological examinations. As examined in flimsy film morphology of AQ01, there is development of intercalated organization of nanowires which frames the pathways for the productive vehicle of charge transporters.

Thusly, we property the high versatility of AQ01 (when contrasted with AQ02) in flimsy film gadgets because of ideal morphology.

CONCLUSIONS

Few chose Imidazoanthraquinone subsidiaries (AQ01-AQ07) were blended and described, where intensifies AQ01 and AQ02 were chosen for additional investigations. These mixtures showed charge move and conglomeration properties. XRD results demonstrated the formless idea of these atoms. Morphological examinations showed the arrangement of interconnected nano-congregations in AQ01, while in AQ02, irregular blossom like designs were noticed. Opening versatility of AQ01 is found in the request for ~ 10-4 cm 2/Vs. Key position state dipole second viewed for AQ01 is accepted to be one of the justification the significant distinction in the morphologies of both these materials. DFT estimation of these atoms further gives data on their connection and H-bonding supramolecular congregations. AQ01 showed more grounded prompting supramolecular congregations. High entire versatility of AQ01 connects well with its morphology in slight film. The fluorescence extinguishing (of P3HT) in mix of AQ01/AQ02 with P3HT showed their potential as non-fullerene electron acceptor. Hypothetical outcomes obviously showed noteworthy decrease of dipole second in its connection in enemy of mode. These results assembly structure supported through proposed that to get positive dipole second and morphology, the materials should total like enemy of stacking mode in slender movies. It is satisfying to take note of that these outcomes are in certification with Wither's model on charge transport properties in strong state gadgets. In this manner, we support his model that the atoms with high dipole minutes can likewise be utilized in natural photovoltaic gadgets given that they have a good morphology in slim movies. High dipole snapshot of AQ01 is accepted to be useful in exaction separation at interface, which makes them possible possibility for BHJ sun based cells.

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