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PII: S0040-4039(16)30572-X
DOI: http://dx.doi.org/10.1016/j.tetlet.2016.05.049
Reference: TETL 47668

To appear in: *Tetrahedron Letters*

Received Date: 19 March 2016
Revised Date: 8 May 2016
Accepted Date: 13 May 2016

Please cite this article as: Wu, S., Li, S., Li, C-Z., Shi, M., Chen, H., Chemical modification of AlQ_3 to a potential electron acceptor for solution-processed organic solar cells, *Tetrahedron Letters* (2016), doi: http://dx.doi.org/10.1016/j.tetlet.2016.05.049

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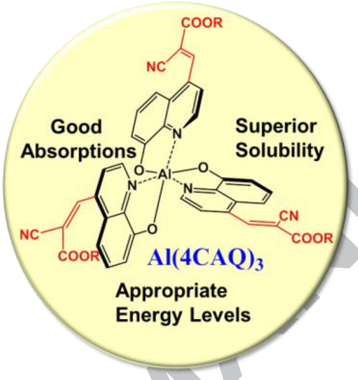

Tetrahedron Letters
journal homepage: www.elsevier.com

Chemical modification of AlQ_3 to a potential electron acceptor for solution-processed organic solar cells

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
AlQ_3
Chemical modification
Non-fullerene acceptors
Organic solar cells

ABSTRACT

In this letter, a new AlQ_3 derivative is designed and synthesized through introducing 2-ethylhexyl cyanoacrylate at C-4 of quinoline ring. The obtained $Al(4CAQ)_3$ shows excellent solubility (> 50 mg/ml) in common solvents. Furthermore, the LUMO energy level of $Al(4CAQ)_3$ is greatly lowered to -3.70 eV, which matches those of donors used in organic solar cells (OSCs). Together with its octahedral molecular geometry and good UV-visible absorptions, $Al(4CAQ)_3$ would be a promising solution-processed electron acceptor for OSCs.

Introduction

Solution-processed bulk heterojunction (BHJ) organic solar cells (OSCs) have attracted much attention for their merits of light weight, flexibility, and low-cost fabrication.[1] In the past years, OSCs have achieved power conversion efficiencies (PCEs) over 10%.[2,3] In OSCs, fullerenes and their derivatives (e.g., [6, 6]-phenyl-C61-butyric acid methyl ester, abbreviated as $PC_{61}BM$) are the dominant electron acceptors owing to their high electron mobilities and isotropic charge transport properties.[4] Nevertheless, fullerene acceptors still suffer from the drawbacks, like tedious purification, poor light absorption, and limited chemical and energetic tunabilities.[5]

The reason why fullerenes and their derivatives work especially well as electron acceptors is that they have spherical structures, thus, when blended with donors to build BHJs, they can form nanoscale phase separation domains and three-dimensional (3D) charge-transporting networks, which are favorable for efficient exciton dissociation and charge transport in OSCs.[6] To work out the superior electron acceptors, a number of small molecular (SM) acceptors have been developed to avoid the defects of fullerenes while reserving their advantages.[4,6-10] Among those materials, 3D or quasi-3D SM acceptors mimicking the fullerene's spherical shape are promising candidates. For example, Yan and co-workers reported a tetraphenylethylene (TPE) core-based 3D SM acceptor, TPE-PDI_4, giving a PCE of 5.53% for the resulting OSCs.[6] Later, Chen and Yan reported a series of tetraphenyl carbon-group core-based 3D SM acceptors, both achieving OSCs with decent PCEs.[4,10] Sauve et al. developed a series of azadipyrromethene complexes with similar distorted tetrahedral geometry as SM acceptors and got a best PCE of 4.1% for the non-fullerene OSCs.[11,12]

Many metal chelates own a twisted octahedral 3D structure. Among these, tris-(8-hydroxyquinoline) aluminum (AlQ_3) is a representative example. AlQ_3 has a central metal Al(III) cation coordinated by three bidentate 8-hydroxyquinoline anions, and it can be vapor-deposited as isolated molecules with the roughly ball-shaped geometry,[13] showing excellent thermal stability, high fluorescent efficiency, and relatively good electron mobility, which lead to the wide uses of AlQ_3 as the emissive and electron-transporting material in organic light-emitting diodes (OLEDs).[14] The above characteristics also make AlQ_3 an attractive building block for the design of new type non-fullerene acceptors for solution-processed OSCs. However, there is no relevant study reported to date. Two key factors hinder the application of AlQ_3 in OSCs: one is its poor solubility in common solvents, the other is its high the lowest unoccupied molecular orbital (LUMO) energy level of -3.0 eV,[15] which mismatches with those of donors in OSCs.

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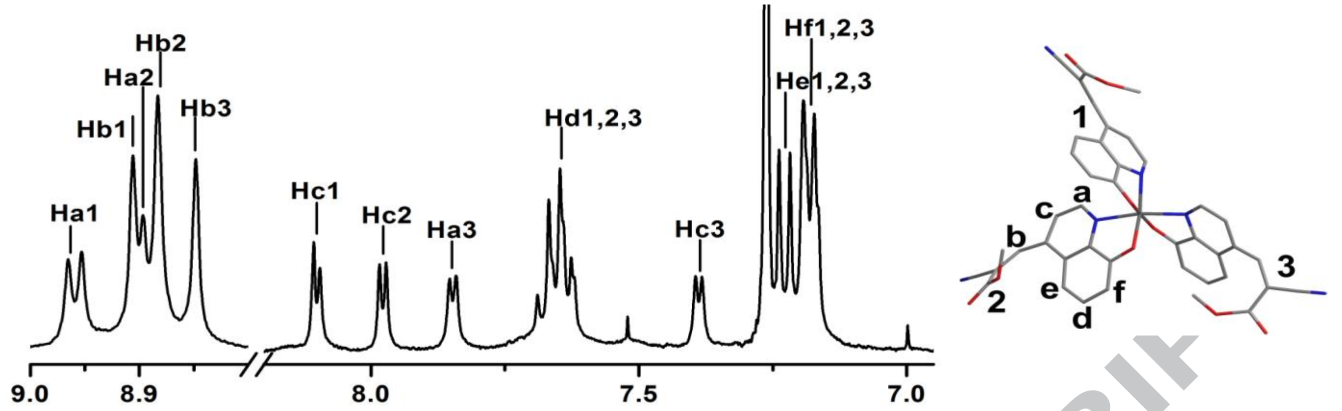
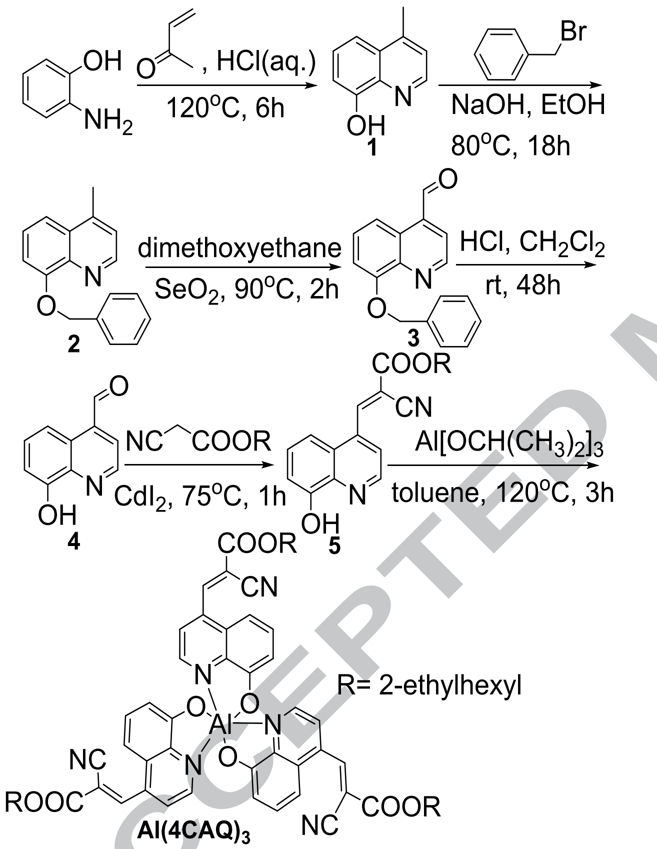


Figure 1. ^{1}H NMR spectrum of **Al(4CAQ)$_3$** in $CDCl_3$ solution. The inset is the steric configuration of *mer*-**Al(4CAQ)$_3$** (2-ethylhexyl is replaced by methyl for clarity), in which three non-equivalent hydroxyquinoline rings are labeled by the numerals 1, 2, and 3, respectively; and the letters a, b, . . ., f represent the positions of H-atoms on the hydroxyquinoline ring.



Scheme 1. Synthetic Route of **Al(4CAQ)$_3$**.

Taking the above considerations into account, we modify AlQ_3 by introducing 2-ethylhexyl cyanoacrylate at the C-4 of quinoline ring. 2-Ethylhexyl cyanoacrylate is selected as the substituent because long branched alkyl (2-ethylhsexyl) is very soluble in organic solvents. Meanwhile, two electron-withdrawing groups (cyano and ester) can significantly reduce the LUMO energy level of AlQ_3. In addition, their conjugation effects with quinoline ring through a double-bond bridge would further lower the LUMO energy level of AlQ_3. And C-4 position is chosen as the substitution site, because the LUMO of AlQ_3 is localized mainly on the pyridyl ring, and C-4 has the highest electron cloud density judging from the molecular simulation of electronic structure for AlQ_3.[16,17] Thereby, an AlQ_3 derivative with the enhanced solubility and appropriate energy levels for the applications in OSCs is expected.

Result and discussion

The target molecule tris-(E)-[4-(2-ethylhexyl cyanoacrylate)-8- hydroxyquinoline] aluminum (**Al(4CAQ)$_3$**) is synthesized in 6-step reactions as shown in Scheme 1. First, 4-methyl-8-hydroxyquinoline (**1**) is prepared through Michael addition of methyl vinyl ketone to 2-aminophenyl, then the hydroxyl group of compound 1 is protected by benzyl (**2**) prior to the oxidation of the methyl at C-4 into the aldehyde group (**3**). After the protecting group of benzyl is removed (**4**), 2-ethylhexyl cyanoacrylate is introduced via Knoevenagel condensation with the aldehyde group, giving the free ligand (E)-4-(2-ethylhexyl cyanoacrylate)-8-hydroxyquinoline (**5**). Finally, the target compound **Al(4CAQ)$_3$** is obtained by complexing the ligand with aluminum isopropoxide. It should be pointed out that other synthetic routes are also tried to synthesize the target molecule **Al(4CAQ)$_3$**, unfortunately, all attempts have failed. For example, before Knoevenagel condensation with 2-ethylhexyl cyanoacetate, we have reacted compound **4** with Al cation to get the AlQ_3 derivative with the aldehyde group at C-4, in order to avoid that the hydroxyl of compound **4** might be destroyed during Knoevenagel reaction. But 4-aldehyde substituted AlQ_3 derivative has very poor solubility and is difficult to purify, so we fail to obtain the target molecule. Therefore, we synthesize compound **5** firstly before its complexation with Al cation. And in order to protect the hydroxyl group on quinoline ring, we choose a solid-phase Knoevenagel condensation using cadmium iodide (CdI_2) as the catalyst.[18]

The chemical structure of the obtained **Al(4CAQ)$_3$** is fully characterized by ^{1}H NMR, ^{13}C NMR, MS, and elemental analysis (Supplementary data). From ^{1}H NMR spectrum (Fig. 1), it is obviously observed that **Al(4CAQ)$_3$** exists as meridional isomer, in which three hydroquinoline ligands are inequivalent by geometric symmetry, i.e. each ligand is distinguishable, leading to the splitting of the NMR peaks for each hydrogen atom.[17,19] And as predicted, **Al(4CAQ)$_3$** can be well dissolved in chloroform, dichloromethane, chlorobenzene et.al., and the solubilities in the above solvents are all more than 50 mg/ml. It even can be dissolved in hexane and ethanol. The thermal properties of **Al(4CAQ)$_3$** are investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in a nitrogen atmosphere (Supplementary data). As shown in Fig. S1, **Al(4CAQ)$_3$** exhibits a thermal decomposition temperature (T_d) of 256 °C with a 5% weight loss and no melting or crystallization peaks during the temperature range of 50-200 °C are observed, indicating that **Al(4CAQ)$_3$** is an amorphous solid.

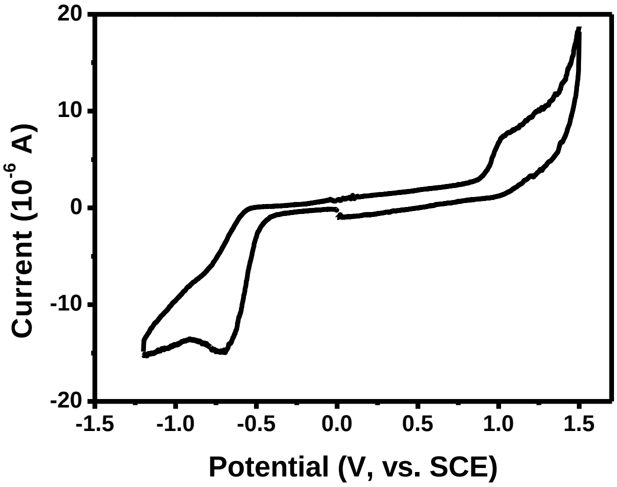


Figure 2. Cyclic voltammogram of **Al(4CAQ)$_3$** in CH_2Cl_2 soution.

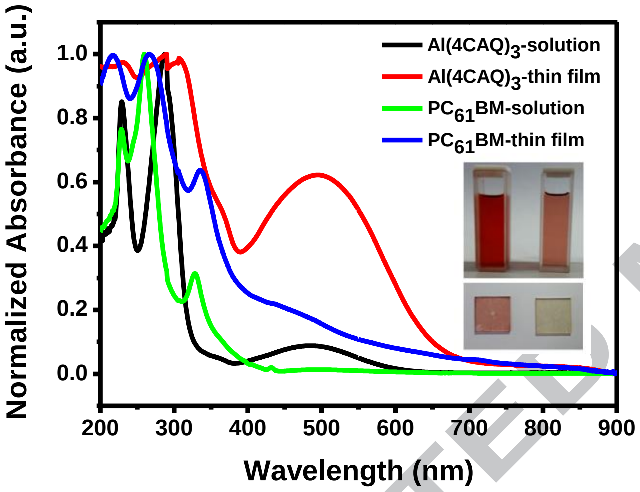


Figure 3. UV-vis absorption spectra of **Al(4CAQ)$_3$** and $PC_{61}BM$ in CH_2Cl_2 solutions and thin films. Insets are the photographs of **Al(4CAQ)$_3$** (left) and $PC_{61}BM$ (right) in CH_2Cl_2 solutions (upper) and thin films (down).

Cyclic voltammetry (CV) measurements are performed to characterize the energy levels of **Al(4CAQ)$_3$**. From the onset oxidation potential (1.01 V versus SCE) and the onset reduction potential (-0.70 V versus SCE) presented in Fig. 2, the highest occupied molecular orbital (HOMO) and LUMO energy levels of **Al(4CAQ)$_3$** are obtained as -5.41 and -3.70 eV, respectively. Compared to the parent molecule AlQ_3, the LUMO energy level of **Al(4CAQ)$_3$** is lowered tremulously by 0.70 eV. It is ascribed mainly to the inductive effect of the electronegative cyano and ester groups, thus it can match donors used in OSCs. Additionally, the HOMO energy level of **Al(4CAQ)$_3$** is 0.29 eV higher than that of AlQ_3 (-5.7 eV),[15] which can be attributed to the conjugation effect of 2-ethylhexyl cyanoacrylate with quinoline ring. The narrowed band gap of **Al(4CAQ)$_3$** would help improve the light-harvesting capability if it is applied as electron acceptor in OSCs. Fig. 3 depicts UV-vis absorption spectra of **Al(4CAQ)$_3$** in solution and film. It is interesting to see that, the absorptions of **Al(4CAQ)$_3$** has been extended to visible range when compared to those of AlQ_3.[16] And the absorptions of **Al(4CAQ)$_3$** are also much stronger and broader than $PC_{61}BM$. From the absorption band-edge (λ_{onset}) at 686 nm, the optical band gap (E_g^{opt}) of **Al(4CAQ)$_3$** is calculated as 1.81 eV, which is in agreement with the value gotten from CV measurements. These results demonstrate the rationality of our molecular design.

Conclusion

In summary, we design and synthesize a new AlQ_3 derivative, **Al(4CAQ)$_3$**, which has a quasi-spherical octahedral 3D structure and exhibits good thermal stability. The introduction of electron-withdrawing 2-ethylhexyl cyanoacrylate to the C-4 of quinoline ring enables **Al(4CAQ)$_3$** with excellent solubility and appropriate LUMO energy level to pair with donors in OSCs. In addition, **Al(4CAQ)$_3$** has better UV-visible absorptions than $PC_{61}BM$. Therefore, **Al(4CAQ)$_3$** may be a promising non-fullerene acceptor for solution-processed OSCs.

Acknowledgments

The authors would like to gratefully acknowledge the financial support from the National Natural Science Foundation of China (No. 21474088) and the Zhejiang Province Natural Science Foundation (No. LR13E030001). This work is also supported by the Joint NSFC-ISF Research Program, jointly funded by the National Natural Science Foundation of China and the Israel Science Foundation (No. 51561145001).

Supplementary Material

Supplementary data (the experimental section, TGA and DSC curves of **Al(4CAQ)$_3$**, scanned NMR spectra and mass spectra) associated with this article can be found, in the online version.

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Highlights:

- An AlQ_3 derivative $Al(4CAQ)_3$ is designed and synthesized in 6-step reactions.
- $Al(4CAQ)_3$ have three 2-ethylhexyl cyanoacrylate groups at C-4 of quinoline ring.
- $Al(4CAQ)_3$ owns an appropriate LUMO of -3.7 eV to pair with donors in OSCs.
- $Al(4CAQ)_3$ shows excellent solubility and good UV-visible absorptions.
- $Al(4CAQ)_3$ would be a promising non-fullerene acceptor for solution-processed OSCs.