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This is the author's manuscript

Original Citation:

Availability:
This version is available http://hdl.handle.net/2318/138861 since 2016-09-12T11:14:34Z

Published version:
DOI:10.1016/j.renene.2013.06.018

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Near-infrared Absorbing Squaraine Dye with extended $\pi$ conjugation for Dye-sensitized Solar Cells

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Keywords: Dye-sensitized solar cell, Near-infrared, NIR squaraine, DFT calculation

Abstract

A NIR absorbing squaraine dye has been synthesized as a sensitizer for use in dye-sensitized solar cells (DSCs). Following computational calculations, a benzo[cd]indole moiety was selected as an electron-rich heterocyclic component and condensed with indole-based emisquaraine bearing a carboxyl group, as an anchor for their immobilization on TiO$_2$, to obtain an unsymmetrical squaraine with extended absorption due to its extensive $\pi$ conjugation. The cells based on this dye exhibited a spectral response in the near-infrared region over 750 nm in addition to the visible region with a light absorption edge at 900 nm. The cells showed 1.1% efficiency and Incident Photon Current Efficiency (IPCE) of 36% at 800 nm.

1. Introduction

Dye-sensitized solar cells (DSCs) have attracted considerable attention due to their relatively high solar energy conversion efficiency and low cost [1]. State-of-the-art DSCs are currently characterized by solar-to-electric power conversion efficiencies (PCEs), ranging around 350-750 nm, of 10–13%.[2,3] The main limit is the lack of absorption in the far-red/near-IR region limiting further improvement in efficiency. Therefore, development of new sensitizers with extended absorption into the infrared region is essential [4]. Squaraine[5], phthalocyanine[6], cyanine, porphyrin[7] and croconate dyes[8] are well documented for their intense absorption bands in the near infrared region and have recently received considerable attention because of their possible applications such as solar cells[9,10], photodynamic therapy[11], lasers, and optoelectronic devices[12].

Several groups have used near-IR dyes as sensitizers in DSCs obtaining rather low conversion efficiencies. This is mainly due to the formation of aggregates and the difficulty to obtain dyes with appropriate energy levels of the excited states, that is with a LUMO sufficiently high in energy to allow for fast electron injection and a HOMO sufficiently low in energy to allow for
fast regeneration. This is particularly difficult to achieve for near-IR dyes where the $\Delta E_{\text{HOMO-LUMO}}$ has to be maintained as small as possible. Therefore, other strategies have to be adopted to guarantee fast injection and fast regeneration in near-IR dye based cells[13]. Another disadvantage of near-IR dyes is their low stability under thermal stress and in the light-soaking test. Therefore, molecular engineering of near-IR dyes with a high photovoltaic performance and an enhanced stability is necessary[14].

So far NIR sensitization was achieved using a panchromatic ruthenium sensitizer based on $\pi$-conjugated quaterpyridines[15,16] and terpyridine[17] yielding an IPCE from 360 nm up to 920 nm, with 33% efficiency at 800 nm. Nickel bis(dithiolene) complexes, exhibiting intense absorption bands below 400 nm and broad absorption bands with high molar extinction coefficients in the NIR region (700–1100 nm), were also used as DSCs sensitizers but their energy conversion efficiencies were in the range of 0.07–0.11%.[18] A polymer dye was also employed with an absorption peak maximum at 820 nm and showed a cell efficiency of 1.2%.[19]

To date, the best NIR dye reported in literature is a symmetrical cyanine dye with maximum absorption band at around 850 nm[20]. An efficiency as high as 2.3% for the infrared-dye-sensitized solar cell was obtained by adjusting the concentration of deoxycholic acid (DCA) in the dye solution but working with a considerably thick (22-26 µm) TiO$_2$ electrode with a light confinement effect, while under more standard condition the efficiency is around 1%, which is comparable to what we have achieved in this work.

Squaraine dyes showing absorption maximum above 750 nm have been extensively studied as fluorescent probes,[21,22,23,24,25] fluorochromes,[26] photosensitizers in photodynamic therapy,[27] fibre-optic sensors,[28] as well as for their spectroscopic properties.[29,30] Recently, an unsymmetrical squaraine dimer synthesized through condensation on a symmetric bis-indolenine bridge, BSQ01 (with $\lambda_{\text{max}}$ = 730 nm in DMF), was used as sensitizer in DSCs, yielding 17% IPCE, and 1.3% cell efficiency (obtained under 100 mWcm$^{-2}$ illumination intensity)[31]; squarylium dyes with similarly extended $\pi$ conjugated systems, LSQa-c (having $\lambda_{\text{max}}$ in the range between 777 and 800 nm in CHCl$_3$), showed conversion efficiencies up to 2.26%.[32]

In the quest for new dyes having specific properties, it is important to be able to predict and select the characteristics for each proposed structure. We already successfully employed a computational approach to design and evaluate different cyanine dye structures before starting the synthesis process[33]. In the present work we evaluated several unsymmetrical squaraines bearing electron donating groups on one side of the molecule (Fig. 1) in terms of absorption range, in order to identify the most promising NIR absorbing dyes for in cell application. The selected dye, coded VG5, has been then synthesised and tested.

We recently reported a kinetic regeneration study for DSCs based on this novel unsymmetrical squaraine VG5 which shed light on the mechanism and limits to the regeneration rate relative to oxidation potential[34]. Furthermore, measurements of the electron lifetime for a series of VG5 based DSCs with varying free iodine concentration contributed to elucidate the
mechanism of electron recombination to the electrolyte in DSCs based on the iodide/triiodide redox couple [13]. We note that in a recent work, a similar squaraine dye was published, called SQ2, which exhibits comparable spectroscopic, electrochemical and photovoltaic properties but with lower short circuit photocurrent and IPCE.[35]

In this paper we report the results of the computational screening on various squaraine dyes and the synthesis, spectroscopic, electrochemical and photoelectrochemical characterization of this squaraine dye, VG5, which exhibits an atypical broad absorption band in the NIR region ranging from 600 to 850 nm. This squaraine was designed using 5-carboxy-2,3,3-trimethyl indolenine as an anchoring moiety, which showed promising efficiency results,[36] and an N-alkylbenzo[cd]indol-1-ium, known for extending absorption to the NIR region, due to its large π conjugation.[37]

2. Experimental details

2.1 Computational analysis

The work was carried out within the Density Functional Theory (DFT) framework[38]. All dyes structures have been first fully optimized for the electronic ground state and then the optical properties have been calculated. The calculation of vertical excitation energy (VEE) and the oscillator strength of low-lying singlet excited state were carried out at the equilibrium geometry using Time Dependent DFT (TD-DFT)[39]. This method makes excited states calculations affordable for medium to large size molecules, but tends to overestimate transition energies; yet trends and comparison between parent molecules are very reliable. The screening over the entire set has been performed using the B3LYP exchange – correlation functional[40] and a standard 6-311G(d) triple zeta basis set. Further analysis on the better performing candidate, VG5, were carried on using the CAM-B3LYP functional[41], i.e. the B3LYP functional modified by Handy and coworkers using the Coulomb-attenuating method, to allow for the partial charge transfer nature of the electronic states of these type of molecules. All calculations have been performed using the Gaussian software[42].

2.2 Synthesis

Column chromatography was performed on Sigma Aldrich silica gel 60 (70-230 mesh ASTM). TLC was performed on Fluka silica gel TLC-PET foils GF 254, particle size 25 mm, medium pore diameter 60 A. Petroleum ether (PE) refers to the fraction boiling in the range 40–60°C. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance 200 spectrometer at 200 MHz and 50 MHz, respectively, in DMSO-d₆. Mass spectra were recorded on a Thermo Finnigan Advantage Max Ion Trap Spectrometer equipped with an electrospray ion source (ESI) in positive or negative ion acquiring mode. Commercially available reagents and solvents were purchased from Aldrich and used without further purification.
Compounds 2-10 (Scheme 1) were synthesized by slightly modification of literature methods.[5, 31, 43, 44, 45, 46] Detailed synthetic procedures and characterizations are available in the Supporting Information.

(E)-2-((E)-(5-carboxy-3,3-dimethyl-1-octylindolin-2-ylidene)methyl)-4-((1-ethylbenz[cd]indol-2-yl)methylene)-3-oxociclobut-1-enolate (VG5): 10 (0.200 g, 0.455 mmol) and 6 (0.135 g, 0.455 mmol) were heated under reflux in butanol/benzene (1:1, 40 mL) in a Dean-Stark apparatus for 3 h. Evaporation followed by flash chromatography (CHCl₃/CH₃OH 9:1) yielded product 11 (0.027 g, yield = 10%).

MS (ESI): m/z 587 [M-1]

1H-NMR (CDCl₃): δ = 0.79 (t, J=6.00 Hz, 3H, N-(CH₂)₇-CH₃), 1.18 (m, 12H, 6 CH₂), 1.37 (m, 3H, NCH₂CH₃), 1.78 (s, 6H, 2 CH₃), 3.99 (m, 2H, NCH₂), 4.16 (m, 2H, NCH₂), 6.04 (s, 1H, CH), 6.27 (s, 1H, CH), 6.96 (t, J=6.00 Hz, 2H, H₅), 7.44 (m, 2H, H₅), 7.75 (t, J=6.00 Hz, 2H, H₅), 8.01 (m, 1H, H₅), 9.08 (m, 1H, H₅)

13C-NMR (CDCl₃): δ 13.60, 13.87, 19.09, 22.37, 26.79, 28.90, 29.12, 30.63, 31.51, 38.40, 43.79, 48.93, 88.66, 90.63, 106.60, 108.85, 121.44, 123.33, 125.32, 125.64, 128.18, 129.47, 130.23, 140.71, 142.04, 145.94, 151.24, 166.10, 170.10, 177.43, 182.7

2.3 Spectroscopic characterization of VG5

UV-Vis spectra were recorded on a Shimadzu UV-1700 spectrometer using different solvents in order to investigate the solvatochromic behaviour of VG5. A stock solution (3.5 · 10⁻³ M) in dimethylsulphoxide (DMSO) was prepared and dilutions (3.5 · 10⁻⁵ M) in tetrahydrofuran (THF), dichloromethane (DCM), dimethyl sulfoxide (DMSO), acetonitrile (ACN), methanol and ethanol were analysed.

Fluorescence measurements were recorded using a Fluorolog 2 from Jobyn Ivon. The excitation wavelength was set at 710 nm. The range for fluorescence emission recording was from 735 to 1000 nm with slits at 14.7 nm.

2.4 Electrochemical characterization

Voltammetric measurements employed a PC controlled AutoLab PSTAT10 electrochemical workstation and were carried out in an Ar-filled glove box, oxygen and water < 1 ppm. Cyclic Voltammetry and Differential Pulse Voltammetry techniques were used to estimate the redox potentials. CVs were obtained at a scan rate of 1 and 0.1 Vs⁻¹, DPVs were obtained at a Modulation Potential of 50 mV, a Step Potential of 10 mV, a Modulation Time of 50 ms and an Interval Time of 100 ms. Measurements were carried out using 0.1 M TBAPF₆ as supporting electrolyte in dimethylformamide (DMF). Glassy carbon, platinum plate and platinum wire were used as working, counter and quasi-reference electrodes, respectively. At the end of each
measurement, ferrocene was added as internal reference. We have considered the redox couple Fc+/Fc to be located at 0.72 V vs NHE in DMF [47].

2.5 Cell preparation

TiO$_2$ (DSL18NRT) films were tape-cast onto transparent conductive F:SnO$_2$ (FTO) glass substrates, LOF Tec 15. They were heated to 450°C in air for 30 min to give a layer thickness of 14 µm. After heating, a layer of Solaronix Ti300 paste was deposited on the film and heated at 450°C in air for 30 minutes to give a 4 µm thick scattering layer. The standard TiCl$_4$ treatment was applied using a 30 mM TiCl$_4$-tetrahydrofuran (THF) complex in water at 70°C for 30 min. [48] After reheating to 450°C for 30 min, the films were allowed to cool to ~100°C and then immersed in the dye solution for 3h. The dye solution used was 0.26 mM VG5 with 52 mM chenodeoxycholic acid (CDCA) in ethanol. CDCA concentration was optimized to achieve an absorbance of 1. Counter electrodes were prepared by drilling two 0.8 mm holes through FTO glass before platinising them with H$_2$PtCl$_6$ (5nM) in 2-propanol. Cells were sealed with 25 µm Surlyn gasket (Solaronix, Aubonne, Switzerland). Electrolyte was injected into the cells through the holes on the counter electrode. The electrolyte composition was 1M Lithium perchlorate LiClO$_4$, 1M 1-propyl-3-methyl imidazolium iodide (PMMI) and 40mM I$_2$ in 3-methoxypropionitrile (MPN). Holes were sealed with a glass cover slip and Surlyn. The cell active area was 1 cm × 1 cm. Silver paint was applied onto the tin oxide on the four sides of the cells to reduce series resistance.

Transparent conductive F:SnO$_2$ (FTO) glass, LOF Tec 15, was purchased from Hartford Glass (Indiana, USA). TiO$_2$ nanoparticle paste DSL18NRT was purchased from DyeSol (NSW, Australia).

3. Results and Discussion

3.1 Computational analysis

The design focused on the effect of substitutions on the optical properties of the dyes, in particular for the presence of electron donating groups. Unsymmetrical squaraine dyes carrying a –COOH group on one indolenine moiety and an electron rich group on the other have been studied (Fig. 1). The substituents used are: -OCH$_3$ moiety (AD1), -N(CH$_3$)$_2$ in R$_1$ (AD2) and R$_2$ (AD3) position, -NPh$_2$ (AD4) and fused benzene ring (AD5 and AD6).
Results for the vertical excitation energy and the energy of the molecular orbitals involved in the main contributions are collected in Table 1. Only results for the most stable conformers are reported.

**Table 1:** Calculated VEE, oscillator strength and dominant contributions of the main transition of the unsymmetrical dyes AD1-AD6.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Irrep</th>
<th>VEE (nm, eV)</th>
<th>Oscillator strength</th>
<th>Dominant contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>AD1</td>
<td>a1</td>
<td>554 (2.24)</td>
<td>1.56</td>
<td>HOMO -4.82, LUMO -2.59, 98</td>
</tr>
<tr>
<td>AD2</td>
<td>a1</td>
<td>572 (2.17)</td>
<td>1.58</td>
<td>HOMO -4.66, LUMO -2.48, 97</td>
</tr>
<tr>
<td>AD3</td>
<td>a1</td>
<td>564 (2.20)</td>
<td>1.49</td>
<td>HOMO -4.77, LUMO -2.55, 96</td>
</tr>
<tr>
<td>AD4</td>
<td>a1</td>
<td>623 (1.99)</td>
<td>0.54</td>
<td>HOMO-2 -5.87, LUMO -3.00, 69</td>
</tr>
<tr>
<td></td>
<td>a2</td>
<td>622 (1.99)</td>
<td>1.36</td>
<td>HOMO -5.00, LUMO -3.00, 69</td>
</tr>
<tr>
<td>AD5</td>
<td>A</td>
<td>656 (1.89)</td>
<td>1.30</td>
<td>HOMO -4.88, LUMO -3.04, 98</td>
</tr>
<tr>
<td>AD6</td>
<td>a1</td>
<td>561 (2.21)</td>
<td>1.51</td>
<td>HOMO -4.88, LUMO -2.66, 97</td>
</tr>
</tbody>
</table>

Among all dyes, AD5 is the one with the absorption maximum most shifted toward the near IR and has, therefore, been studied in more detail and later synthesised with the code VG5. The difference between model AD5 and the actual molecule VG5 is in the alkyl substituents on the indolenine nitrogens, where both the C₈H₁₇ chain and the ethyl group have been substituted with a methyl moiety. It is known that this kind of substitutions do not affect the results of the calculation, as the alkyl chains are not involved in the delocalized electron distribution, which is responsible for the optical properties of the dye. For this molecule, DFT predicts a planar dye
skeleton, as expected for a large conjugated $\pi$ system, and only small distortions are predicted on the aromatic substituents.

![Figure 2: relaxed structure for VG5.](image)

The Vertical Excitation Energies (VEE) have been calculated using the CAM-B3LYP functional for the first five lowest energy electronic transitions, and are reported in Table 2 together with the oscillator strength, and the description of the molecular orbitals involved in the corresponding transition.

**Table 2:** Calculated VEE, oscillator strength and dominant contributions of the first five lowest energy electronic transitions of dye VG5.

<table>
<thead>
<tr>
<th>Transition</th>
<th>VEE nm (eV)</th>
<th>Oscillator strength</th>
<th>Dominant contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>606 (2.04)</td>
<td>1.43</td>
<td>HOMO</td>
</tr>
<tr>
<td>2</td>
<td>456 (2.71)</td>
<td>0</td>
<td>HOMO-2</td>
</tr>
<tr>
<td>3</td>
<td>349 (3.55)</td>
<td>0.01</td>
<td>HOMO-1</td>
</tr>
<tr>
<td>4</td>
<td>337 (3.68)</td>
<td>0.12</td>
<td>HOMO</td>
</tr>
<tr>
<td>5</td>
<td>331 (3.73)</td>
<td>0</td>
<td>HOMO-5</td>
</tr>
</tbody>
</table>

The absorption spectra of AD5 (VG5) shows a strong, optically allowed, band at 606 nm, corresponding to the HOMO→LUMO transition, and a less intense band at 337 nm roughly corresponding to the HOMO→LUMO+1 transition. As it can be noted from table 1 the other electronic transitions have a negligible oscillator strength. The molecular orbitals involved in the main adsorption transitions are shown in Figure 3.

![Figure 3: Representation of frontiers orbitals involved in adsorption spectra.](image)
The strong discrepancy between the observed (about 770 nm, see section 3.3) and the calculated absorption energies is a well documented problem of TD-DFT theory which tends to overestimate the electronic transitions energies for such systems, yet providing a qualitatively correct picture of the excitation process.

It can be noted that the HOMO→LUMO transition corresponds to a partial migration of the electronic charge from the squarainic ring to the benzoindolenine moiety. On the other hand, transitions involving the HOMO and the LUMO+1 molecular orbitals are a clear-cut charge transfer transitions toward the carboxylic group.

Finally, it is worth noting that the model employed does not include Frank-Condon effects and cannot reproduce the other peaks experimentally observed which correspond to vibronic bands.

3.2 Synthesis of VG5

VG5 was synthesized by condensation of benzoindolenine salt 6 with emisquaraine 10. 6 was prepared according to literature method from naphthostyril 1, via methylation of thionaphthostyril 2 [43,44], protection with Meldrum’s acid [45] followed by alkylation and deprotection [46]. A complete characterization of all the intermediates has been accomplished.

3.3 Photochemical and electrochemical properties of VG5

As reported in Figure 4a, the Vis/NIR absorption spectrum of VG5 in EtOH shows one shoulder and an absorption maximum at 722 nm and 768 nm, respectively. The solvatochromic shift of VG5 was studied and is reported in Figure 4b and Table 3. UV-Vis absorption as well as steady-state fluorescence emission spectra show, in general, a negative solvatochromism which results from a higher polarity of the ground state with respect to the excited state.[49,50] The red-shift of 62 nm from BSQ01 [31] absorption maximum at 730 nm in DMF is consistent with the expected effect of extending conjugation.
Figure 4: a) absorbance and fluorescence emission spectra in ethanol and b) solvatochromism of VG5.

<table>
<thead>
<tr>
<th>Table 3: Spectroscopic properties of the solvatochromism of VG5.</th>
</tr>
</thead>
<tbody>
<tr>
<td>shoulder</td>
</tr>
<tr>
<td>λ_{max} [nm]</td>
</tr>
<tr>
<td>THF</td>
</tr>
<tr>
<td>DCM</td>
</tr>
<tr>
<td>DMSO</td>
</tr>
<tr>
<td>ACN</td>
</tr>
<tr>
<td>EtOH</td>
</tr>
<tr>
<td>MeOH</td>
</tr>
</tbody>
</table>

The oxidation and reduction potentials of the dye are located respectively at +0.10 V and −1.16 V vs Fc+/Fc couple. The cyclic voltammogram shows quasi-reversible peaks (Fig. 5). Moreover, as can be observed from the DPV (dark blue curve), inducing a second reduction of the dye (−1.95 V vs Fc) gives rise to a decomposition product, which is oxidized at about −0.5 V vs Fc. The measured redox potential is used as an estimation of E^0. We assumed that the first oxidation potential (E^0_{ox}) and reduction potential (E^0_{red}) correspond to the HOMO and, with a larger approximation, to LUMO levels of the dye. Therefore, using the conversion factor of Fc+/Fc 0.72 V vs NHE, the HOMO and LUMO levels are located at 0.82 and −0.44 V versus NHE for VG5. In the literature, the LUMO is also calculated by subtracting the value of the electrochemical potential of this dye from the value of the oxidation potential E^0_{ox}. This method provides the LUMO of the dye located at even lower levels. The value of the electrochemical potential of this dye is consistent for a possible fast regeneration while the injection can be affected from the fact that VG5 LUMO is too low compared to the TiO_2 conduction band.
3.4 Cell performance

The cell I-V characteristics were measured using a 150W Xenon lamp filtered to simulate AM 1.5. The cell I-V plot for both 1 sun and dark short circuit current is shown in figure 6, as shown the short circuit maximum photocurrent (Jsc), the Open-Circuit voltage (Voc), the fill factor (FF) and the overall efficiency at AM 1.5 conditions were respectively 7.29 mA cm$^{-2}$, 0.35V, 0.43 and 1.10%. The low voltage for this cell is due to the very high Lithium content of the electrolyte (1M), and the absence of base. This composition was required to lower the TiO$_2$ conduction band edge to allow injection from the low lying LUMO of this dye. The LUMO lies at $-0.44$V vs NHE, 0.26V below the conduction band edge in standard solvents ($-0.7$V vs NHE). The voltage loss with respect to the standard cells with N719 dye ($-0.75$V) reflects mainly the change in electrolyte, though there may also be a contribution from enhanced recombination.
IPCE measurements were performed using a shuttered monochromated light source where the intensity was calibrated using a UV-enhanced silicon photodiode. Incident photon conversion efficiency is plotted against the absorption spectrum of VG5. The implied “1 sun” photocurrent calculated by integrating the IPCE with the AM1.5 spectral intensity, is 6.7 mA cm\(^{-2}\), which is quite close to the 7 mA cm\(^{-2}\) measured. The dye shows a maximum quantum efficiency of 36% at 800 nm. As virtually all light was absorbed at this wavelength, this also corresponds to an absorbed photon to current efficiency (APCE) of 36%. Interestingly, the APCE at wavelengths below 624 appears to be larger, even allowing for increased absorption in the cell due to the scattering layer. This result is in line with the calculated DFT data, for example the enhanced APCE at 440 nm can be explained by the participation in the transition of the HOMO−2 and LUMO+1 molecular orbitals; as noted above, this transition involves a D-π-A charge transfer across the molecule which gives the correct directionality for electron injection. The absorption spectrum of the dye solution is included for comparison (Fig. 7). In the IPCE spectrum, some peaks have clearly shifted, most likely due to the change in solvent and solvatochromism of the dye.
The design, synthesis and characterization, as well as the full characterization of all the intermediates, of a near infrared dye, coded VG5, was accomplished. This dye was selected among a variety of candidates as NIR absorbing dyes: the screening was performed using a computational approach, thus evaluating the optical properties of a range of promising dye structures using a TD-DFT approach prior the synthetic steps. The selected dye was then spectroscopically and electrochemically characterized showing a negative solvatochromism and a presumed fast regeneration but a low LUMO level. DSCs based on TiO2 photoelectrodes dyed with VG5 were fabricated and the photovoltaic properties were characterized under AM 1.5 irradiation. An overall energy efficiency of 1.1% and IPCE of 36% at 800 nm were achieved with a standard TiO2 layer. This result shed light to possible future NIR structures to be used as sensitizers for DSCs. Actually, even if VG5 has shown a limited efficiency, its strong absorption at 780 nm makes it a useful system for fundamental mechanistic studies on NIR dyes [13,34].

Acknowledgements
CM, JP and C.Benzi acknowledge financial support by Innovasol EU project (227057-2), NB and C.Barolo acknowledge DyeCells project (grant code 121) from Ministero dell’Ambiente e della Tutela del Territorio e del Mare. NB thanks MIUR for partial funding her research grant. SM and AA acknowledge support from the Imperial College UROP Bursary and the Alan Howard Scholarship for Energy Futures. We thank Dr. Davide Di Censo for electrochemical measurements and fruitful discussion and Ms. Ada Ferri for her valuable help.
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