Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Recent Developments in Tetrathiafulvalene and Dithiafulvalene based Metal–Free Organic Sensitizers for Dye-sensitized solar cells: A Mini Review

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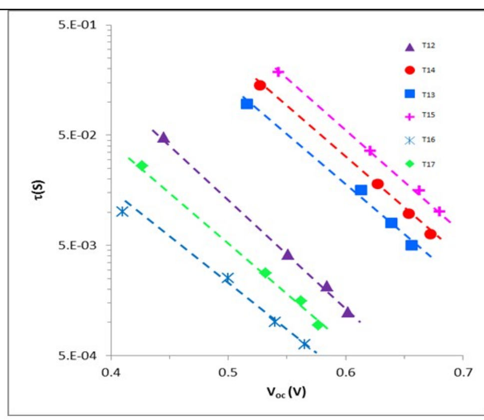
Table 1: electronic life time

Dye	τ_e	REFERENCE
T1	2.3 ms	54
T2	256us	54
T3	494us	54
T4	-------------	55
T5	-------------	59
T6	-------------	59
T7	-------------	59
T8	-------------	59
T9	-------------	60
T10	-------------	60
T11	-------------	60
T12	(see figure below)	56
T13		56
T14		56
T15		56
T16		56
T17		56



Electron lifetime (t) as a function of Voc for DSSCs sensitized with G1-G6. Electron lifetime was measured by means of intensity-modulated photovoltage spectroscopy.

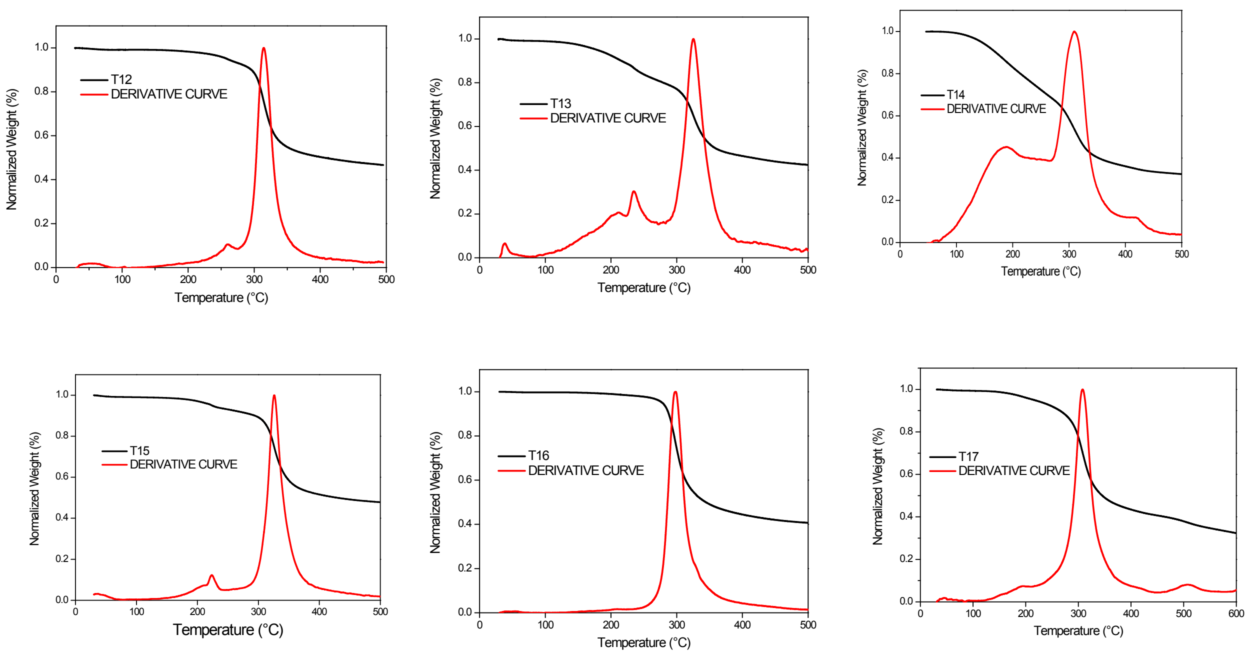
T12 and T13 Electronic Lifetime Order :T13>T12

T14-T17 Electronic Lifetime Order:T15 > T14 > T17 > T16

Thermal stability

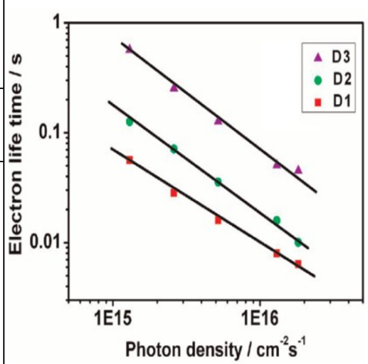
T12-T17: The advantage of this invention is that these classes of sensitizers are thermally stable up to 200 °C to 250 °C, which is one of the requisite of DSSC technology.

TG/DTG Curves of T12-T17 with a heating rate of 10 °C min^{-1} under nitrogen atmosphere.



Thermal stability of dyes, which are essential for roof top applications. It is known in literature that tetrathiafulvalene derivatives are thermally stable. We have carried out thermogravimetric analysis of all dyes it is apparent that the thermal behaviour of **T12** and **T13** are stable up to 250 ºC, **T14** and **T15** are stable up to 200 ºC, whereas T16 and **T17** are stable up to 260 ºC. The initial weight loss between 200 to 260 ºC (5.20%) is due to the removal moisture. Among metal-free organic sensitizers based DSSC, tetrathiafulavalene based molecules are thermally stable and probable candidates for rooftop applications. the similar trend in thermal stability of remaining sensitizers. It is clear from the thermal data that these dyes are highly durable for long standing outdoor applications.

Table 2: electronic life time

<table>
<tr><th>Dye</th><th>τ_e</th><th>Ref.</th></tr>
<tr><td>D1</td><td rowspan="3">

The electron lifetimes of the three sensitizers are positively correlated with their π-bridge lengths. In particular, D3 has the longest π-bridge and hence holds the longest electron lifetime which is almost 10-fold higher than that of D1. This result shows that for the sensitizer series studied here the electron lifetime is mainly determined by the recombination with the contiguous electrolyte as commonly believed. Plausibly, with the increasing length of the π-bridge, it would become increasingly more difficult for the injected electron in the TiO_2 CB to recombine with the redox electrolyte due to the formation of a thicker dye block layer. Additionally, electron recombination with the photo-oxidized adsorbed sensitizers could also be decreased with increasing π-bridge length simply due to the ionized HOMO being more spatially removed from the TiO_2 substrate. This naturally explains the highest Voc (0.83 V) for D3.</td><td>61</td></tr>
<tr><td>D2</td><td>61</td></tr>
<tr><td>D3</td><td>61</td></tr>
<tr><td>D4</td><td>19.21 ms</td><td>62</td></tr>
<tr><td>D5</td><td>16.18 ms</td><td>63</td></tr>
<tr><td>D6</td><td>19.89 ms</td><td>63</td></tr>
<tr><td>D7</td><td>19.15 ms</td><td>64</td></tr>
<tr><td>D8</td><td>24.88 ms</td><td>64</td></tr>
<tr><td>D9</td><td>-----------------</td><td>65</td></tr>
<tr><td>D10</td><td>-----------------</td><td>65</td></tr>
<tr><td>D11</td><td>-----------------</td><td>65</td></tr>
<tr><td>D12</td><td>-----------------</td><td>65</td></tr>
<tr><td>D13</td><td>-----------------</td><td>65</td></tr>
<tr><td>D14</td><td>-----------------</td><td>65</td></tr>
<tr><td>D15</td><td>-----------------</td><td>65</td></tr>
<tr><td>D16</td><td>-----------------</td><td>66</td></tr>
<tr><td>D17</td><td>-----------------</td><td>66</td></tr>
<tr><td>D18</td><td rowspan="3">The order of electron time (τ_e) would be in reverse with that of the peak frequency of lower-frequency range (f) in their devices. So D18 ~ 20 dyes display longer electron lifetime than that of DP-1 in their cells. The DSSC device of D21 with the longest electron lifetime demonstrates the best photovoltaic performance.</td><td>67</td></tr>
<tr><td>D19</td><td>67</td></tr>
<tr><td>D20</td><td>67</td></tr>
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D21		67