

1 **Molecular Engineering of Cyanine Dyes to Design a**
2 **Panchromatic Response in Co-sensitized Dye-Sensitized**
3 **Solar Cells**

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19 Cyanines are optically tunable dyes with high molar extinction coefficients, suitable for
20 applications in co-sensitized dye-sensitized solar cells (DSCs); yet, barely thus applied.
21 This might be due to the lack of a rational molecular design strategy that efficiently
22 exploits cyanine properties. This study computationally re-designs these dyes, to broaden
23 their optical absorption spectrum and create dye··TiO₂ binding and co-sensitization
24 functionality. This is achieved via a stepwise molecular engineering approach. Firstly,
25 the structural and optical properties of four parent dyes are experimentally and
26 computationally investigated: 3,3'-diethyloxycarbocyanine iodide, 3,3'-
27 diethylthiacarbocyanine iodide, 3,3'-diethylthiadiazocarbocyanine iodide and 3,3'-
28 diethylthiatricarbocyanine iodide. Secondly, the molecules are theoretically modified
29 and their energetics are analyzed and compared to the parent dyes. A dye··TiO₂
30 anchoring group (carboxylic or cyanoacrylic acid), absent from the parent dyes, is
31 chemically substituted at different molecular positions to investigate changes in optical
32 absorption. We find that cyanoacrylic acid substitution at the para-quinoidal position
33 affects the absorption wavelength of all parent dyes, with an optimal bathochromic shift
34 of ca. 40 nm. The theoretical lengthening of the polymethine chain is also shown to effect
35 dye absorption. Two molecularly engineered dyes are proposed as promising co-
36 sensitizers. Corresponding dye··TiO₂ adsorption energy calculations corroborate their
37 applicability, demonstrating the potential of cyanine dyes in DSC research.

38

39 1 Introduction

40 Dye-sensitized solar cells (DSCs) are becoming increasingly attractive for harvesting solar
41 energy. The interest in this photovoltaic (PV) technology is driven, in part, by the low costs of
42 production, stability and flexibility of design compared to other PV technologies.¹⁴ The
43 capability of controlling their color and transparency gives them niche potential to be
44 engineered in "smart windows" ~~22~~⁴⁴ and they already outperform competitors in indoor
45 applications.¹ Yet, since their first application ~~55~~, DSCs have not seen a satisfactory rise in
46 power conversion efficiency. However, recent developments have reported DSCs with 13%
47 efficiency, achieved via a zinc-centred porphyrin dye ~~66~~, and a record-breaking cell with
48 14.3% efficiency ~~77~~, involving the co-sensitization of two organic dyes.

49 The most commonly used sensitizers in DSCs are ruthenium-based complexes or dyes
50 containing precious metals. Their strength chemically lies in metal-to-ligand charge transfer
51 (MLCT), which broadens the optical absorption spectrum across most visible wavelengths.¹⁴
52 ~~88~~ ~~99~~ However, metal-free organic dyes have a number of advantages over metal-containing
53 dyes, which makes them attractive for use in DSCs. By comparison, they are cheap, widely
54 available and more environmentally sound. They have higher molar extinction coefficients (ϵ),
55 which allows for greater light absorption at a given wavelength and they have readily tunable
56 absorption wavelengths and high molecular design flexibility.¹⁴ ~~10+0~~ ~~11+1~~ Furthermore, they
57 have found recent advances in devices' durability by chemically altering the molecular
58 structure¹² and have found applications in flexible DSCs.¹³

59 Despite this, a major disadvantage of organic dyes is their narrow absorption spectra. This
60 substantially limits the light-harvesting capabilities of an associated DSC device, hampering

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61 the short-circuit current density and power conversion efficiency. An effective solution to this
62 problem is to co-sensitize a TiO₂ film with multiple dyes possessing different optical
63 absorption spectra, thereby generating a panchromatic dye/TiO₂ working electrode.¹⁴ This co-
64 sensitization technique has found increasing popularity over the past few years, thanks to its
65 promising enhanced light harvesting, and has generated the current world record in DSC
66 efficiency.⁷⁷ In order to successfully achieve panchromatic optical absorption, the
67 combination of dyes employed in the co-sensitized solar cell must be carefully selected.
68 Problems such as chemical compatibility and competition between dye molecules upon
69 sensitization greatly hinder DSC performance. Molecular engineering of the sensitizers
70 therefore opens an interesting prospect to rationally design a reliable combination of dyes for
71 co-sensitization.

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72 The molecular design of new dyes is restricted by two specific requirements that a
73 sensitizer must meet in order to function properly in a DSC: (i) The lowest-unoccupied
74 molecular-orbital (LUMO) energy of the dye must exceed the conduction-band energy of TiO₂
75 to favor unidirectional charge injection into the TiO₂. Likewise, the highest-occupied
76 molecular-orbital (HOMO) energy of the dye must be lower than the electrolyte redox energy
77 (E_{redox}) to successfully regenerate the dye after charge injection. A dye whose electronic
78 structure does not meet these energetic requirements will fail to generate current in a DSC. (ii)
79 The dye must possess an anchoring group that both stabilizes the dye on the TiO₂ surface and
80 allows for charge injection. The primal carboxylic acid, -COOH, and cyanoacrylic acid groups
81 are, by far, the two most popular anchors.¹¹

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82 Other structure-property relationships have also been shown to benefit the function of
83 DSCs. Firstly, dyes with a “push-pull” molecular framework are easier to design for use in

84 DSCs. Here, an electron-donor moiety (D) is separated from an electron-acceptor group (A)
85 via a π -linker, usually consisting of a π -conjugated bridge (D- π -A). The acceptor is typically
86 situated in, or around, the anchoring group to ease charge injection. This D- π -A molecular dye
87 architecture allows for fine tuning of its molar extinction coefficient, maximum optical
88 absorption wavelength, and HOMO/LUMO energy levels, whilst enabling directed intra-
89 molecular charge transfer (ICT). Furthermore, recent studies claim that separating the acceptor
90 group from the anchoring group through adding an extra π -conjugation unit (to form the D- π -
91 A- π -anchor motif) can lead to over 6.5 times higher power conversion efficiencies compared
92 to the simple (D- π -A) structure.¹⁵ Secondly, high molar extinction coefficients, ϵ , permit the
93 use of thinner films of TiO₂ in the DSC working electrode, reducing unfavorable electron-
94 recombination processes with the electrolyte.¹⁶ Thirdly, a combination of dyes that maximizes
95 light harvesting in both the visible and near-IR region of the optical absorption spectrum is
96 advantageous in order to achieve a panchromatic response, which increases the short-circuit
97 current density in DSCs.^{17, 18}

98 Cyanines are a chemical family of well studied "push-pull" dyes which meet many of the
99 structure-property requirements for DSC dyes. These chromophores have dominated the field
100 of photography over the past century and have recently displayed potential as functional
101 materials for a wide range of applications, such as lasers, optical data storage, photorefractive
102 technology, antitumor agents, probes for biological systems and light harvesting devices.¹⁹
103 Their high molar extinction coefficients and simplicity of optical tuning makes them prime
104 candidates for DSCs, particularly within the realm of co-sensitization. The generic cyanine
105 consists of two nitrogen centers, located within hetero-cycles, one of which is positively
106 charged and linked to the other nitrogen by a polymethine bridge that consists of an odd

107 number of carbon atoms. The length of this π -conjugated chain constitutes the biggest
108 contribution to the optical absorption spectrum of the dye. For example, the extension of the
109 chromophore by one vinylene moiety (-CH=CH-) causes a bathochromic shift of
110 approximately 100 nm in the absorption spectrum.¹⁹

111 In the context of DSCs, cyanine dyes have not been extensively used as sensitizers or co-
112 sensitizers. The earliest attempt to use cyanines in a DSC involves the co-sensitization of two
113 cyanine dyes with an oxygen and sulfur center, respectively.²⁰ This study realized the
114 importance of using dyes with high molar extinction coefficients, which leads to thinner TiO₂
115 films and reduced recombination. Subsequent studies by Sayama et al. analysed DSCs co-
116 sensitized with three cyanine dyes, focusing on the importance of co-sensitization for
117 suppressing detrimental dye aggregation.^{21,22} An investigation of two carboxylated cyanine
118 dyes reported the formation of a tightly-packed mono-layer of cyanines, upon co-sensitization,
119 reducing electron recombination with the electrolyte.²³ Despite these experimental efforts to
120 produce efficient co-sensitized DSCs with cyanine dyes, the reported power conversion
121 efficiencies were between 2.5% and 3.5%, which is an unsatisfactory result in comparison
122 with other organic dyes. Although these particular cyanine-based DSC trials did not meet the
123 expectations conveyed by the aforementioned intrinsic optical properties that suggest their
124 potential for DSC operation, a more systematic approach may be able to rectify this deficit.

125 Through a series of molecular adjustments, cyanines can be converted into efficient co-
126 sensitizers for a DSC device. A key advantage of applying molecular engineering strategies to
127 design co-sensitized DSCs lies in the capability to tailor a panchromatic response of the DSC
128 by selecting a pair of (or more) dyes which exhibit complementary optical absorption spectra
129 that, when combined, emulate the solar spectrum of light. For example, a panchromatic

130 response can be achieved using a pair of dyes designed to exhibit optical absorption at
131 opposite ends of the UV/vis spectral bandwidth to each other. Another beneficial feature of
132 molecular engineering is the ability to shift optical absorption towards IR wavelengths. Near-
133 IR is a rarely used portion of the solar spectrum for light harvesting and it makes possible
134 translucent DSC devices with good optical penetration characteristics.²⁴ Furthermore, co-
135 sensitization of several chemical derivatives of the same parent dye tends to reduce the
136 possibility of employing chemically incompatible dyes within the same DSC. To this end, four
137 carbocyanines bearing complementary absorption spectra are herein investigated: 3,3'-
138 diethylloxycarbocyanine iodide (**1**), 3,3'-diethylthiacarbocyanine iodide (**2**), 3,3'-
139 diethylthiadibenzocarbocyanine iodide (**3**) and 3,3'-diethylthiatricarbocyanine iodide (**4**).

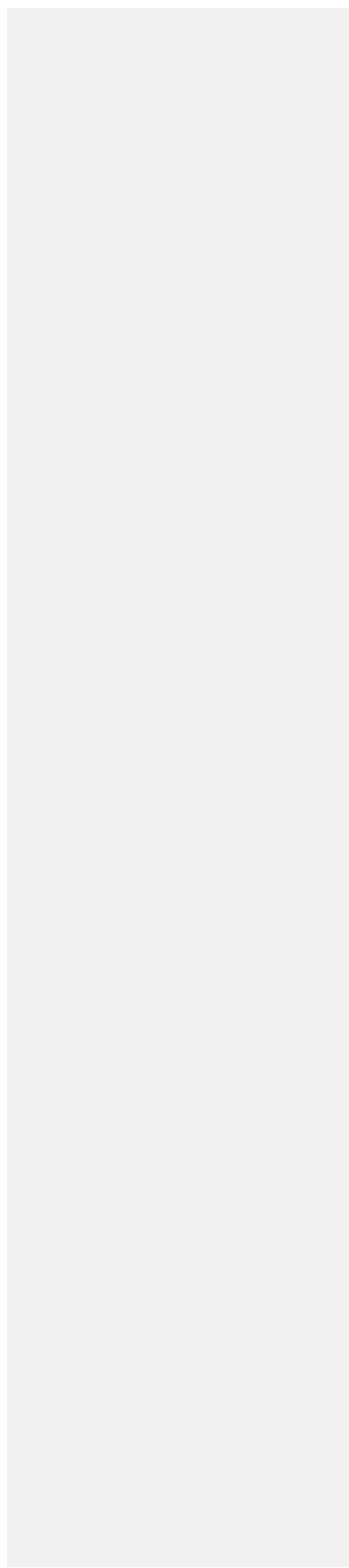
140 This study involves the re-engineering of four cyanine-based laser dye molecules, **1-4**, to
141 generate DSC dyes via (i) adding a DSC-suitable anchoring group at an appropriate
142 substitution point on each molecule to achieve a strong dye···TiO₂ binding while affording
143 ICT that promotes an advantageous shift in optical absorption energy; (ii) varying the length
144 of the polymethine bridge in order to further tune the absorption energy. Experimental and
145 computational methods are first employed to characterize the structure and optical properties
146 of the parent dyes. In this respect, single-crystal X-ray diffraction on **1-4** is used to obtain their
147 solid-state structure, while solution UV/vis absorption spectroscopy enables the determination
148 of their absorption profiles. The initial data from these experiments serve as the pre-requisite
149 knowledge-base for molecular engineering of cyanine-based DSC dyes. The computational
150 efforts exploit density functional theory (DFT), time-dependent density functional theory (TD-
151 DFT) and Laplace transformed density fitted local CC2 (LT-DF-LCC2) calculations. DFT
152 predicts HOMO and LUMO energy levels of each molecule and the ICT properties. TD-DFT

153 and LT-DF-LCC2 simulate the optical transitions of each dye. The best dye candidates, as
154 judged by molecular structure and energy qualifiers, are taken forward for additional
155 computational studies whereby dyes are adsorbed on a TiO_2 surface as represented by a
156 $(\text{TiO}_2)_9$ cluster. This modeling permits monitoring of plausible changes in the optoelectronic
157 properties of the dye at the dye- $\cdot\cdot\cdot\text{TiO}_2$ interface and enumeration of the associated adsorption
158 energies. These molecular engineering steps are summarized in Figure 1 and Figure 2, the
159 result of which is the material prediction of a pair of cyanine-based DSC co-sensitizers.

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162 Figure 1: Schematics of the molecular engineering strategy. Experiments are in yellow,
163 while computational methods are in green.



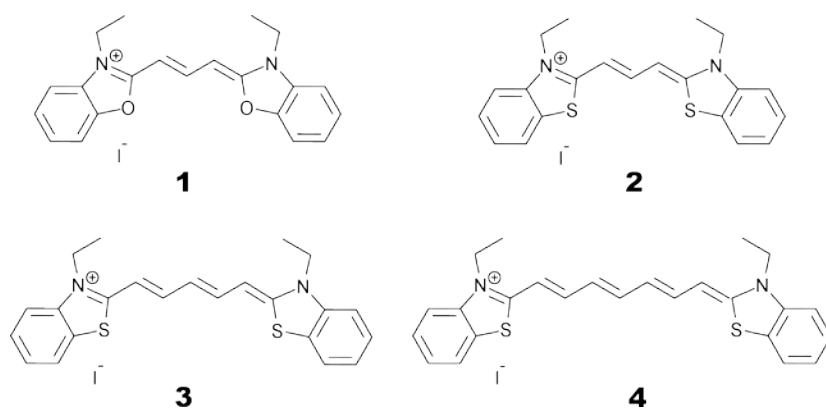
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165 Figure 2: Schematic of the relationships between experimental and computational methods for
166 the optoelectronic studies on the parent dyes, as illustrated for **1**. Experiments are in yellow,
167 while computational methods are in green boxes.

168 **2 Experimental and Computational Methods**

169 **2.1 Materials**

170 Commercially available powders of dyes **1-4** were obtained from Sigma-Aldrich. These
171 compounds are ionic, with I⁻ serving as a neutralizing counter-ion for each dye. Skeletal
172 formulae are shown in Figure 3, showing 3,3'-diethyloxacarbo-cyanine iodide [C₂₁H₂₁N₂O₂][I⁻]
173 as **1**, 3,3'-diethylthiacarbo-cyanine iodide [C₂₁H₂₁N₂S₂][I⁻] as **2**, 3,3'-diethylthiadica-cyanine
174 iodide [C₂₃H₂₃N₂S₂][I⁻] as **3** and 3,3'-diethylthiatricarbo-cyanine iodide [C₂₅H₂₅N₂S₂][I⁻] as **4**.

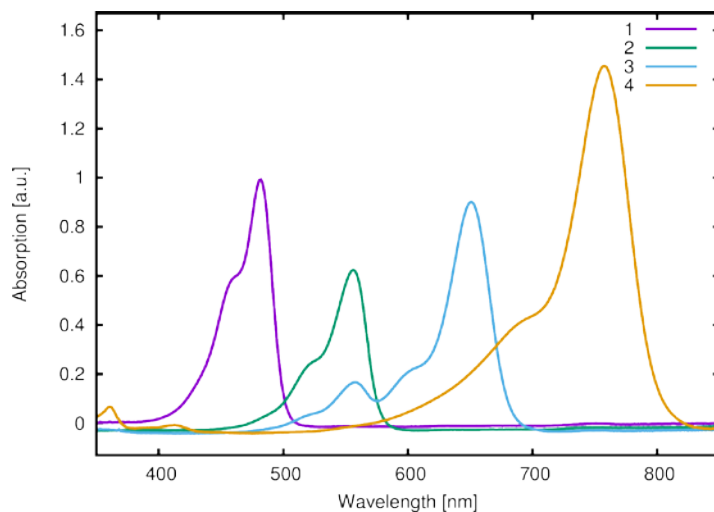


176 Figure 3: Skeletal chemical formulae of the parent dyes **1-4**.

177 **2.2 Single Crystal X-Ray Diffraction**

178 Single crystals of dyes **1-4** were grown by slow evaporation of saturated methanol solutions at
179 room temperature over the course of ten days. The resulting crystals were suitable for single-
180 crystal X-ray diffraction measurements from which their crystal structures were realized.
181 Diffraction data were collected at 120 K for all crystals, using a Rigaku Saturn 724+ CCD
182 diffractometer, equipped with a molybdenum X-ray source ($\lambda_{\text{Mo-K}\alpha} = 0.71073 \text{ \AA}$), SHINE

183 Optics focusing and an Oxford Cryosystems CryostreamPlus open-flow N₂ cooling device.
184 Cell refinement, data collection and integration were undertaken via the Rigaku CrystalClear-
185 SM Expert 2.0 software package ²⁵, and an absorption correction was implemented using
186 ABSCOR.²⁶ Structures were solved by direct methods and refined by full-matrix least-squares
187 methods on F². All refinements were performed using SHELXS.²⁷ Hydrogen atoms were
188 positioned geometrically and refined as riding on their parent atoms. The crystal structure
189 determination of **2** exhibited solvent accessible channels along the crystallographic [001]
190 direction. The disordered solvent molecules therein could not be modeled rationally; hence,
191 the contents were treated as a diffuse contribution to the overall scattering using
192 SQUEEZE/PLATON.²⁸ While the molecular geometry of **3** was clearly resolved from its best-
193 fit crystal structure model, the refinement of this model against the data produced somewhat
194 poor statistical qualifiers. Accordingly, use of this crystal structure of **3** was restricted to its
195 provision of input molecular geometry for DFT calculations where this geometry was
196 computationally optimized. A full summary of crystal data, crystallographic collection and
197 refinement details are provided in Electronic Supplementary Information S.1. and associated
198 deposition material.



199

200 Figure 4: Experimental UV/vis absorption spectra for **1-4**. Data were collected in methanol at
 201 0.01 mM concentration. Spectra have been scaled by a common factor such that the absorption
 202 peaks are normalized with respect to **1**.

203 **2.3 UV/vis Absorption Spectroscopy**

204 UV/vis absorption spectroscopy was performed on a Agilent Cary 300 UV-vis
 205 spectrophotometer. Absorption spectra were recorded in methanol (Figure 4) at a
 206 concentration of 0.01 mM for all dyes. Peak molar extinction coefficients, ϵ , were calculated
 207 using the gradient of the regression line obtained from the measurement of peak absorbance
 208 over five different dye concentrations. Peak absorbance for each concentration was measured
 209 five times in order to spot potential systematic errors and obtain a standard uncertainty on the
 210 measurement. Dye aggregation was studied for dye **3**, as it presented a number of shoulder
 211 peaks which could be attributed to dimer or trimer formation in solution; solution
 212 concentration and the solvent identity were modified in order to control the relative changes in

213 peak intensity. The absorption spectrum of **3** was measured in methanol for 15 concentrations,
214 halving it at every step from 5×10^{-4} M to 3×10^{-8} M and was further measured at 1.5×10^{-5} M in
215 methanol, acetone, dimethyl sulfoxide, acetonitrile and dichloromethane (see Electronic
216 Supplementary Information S.2). A summary of the salient spectral information for all dyes is
217 reported in Table 1.

218 **2.4 Cyclic Voltammetry**

219 Cyclic voltammograms for **1-4** were recorded at scan rates of 25, 50, 75, and 100 mV/s in
220 acetonitrile (0.5 mM) against an Ag/AgCl in KCl reference electrode, using an Autolab
221 PGSTAT101 with a carbon working electrode and a platinum counter electrode. Prior to each
222 measurement, analyte solutions were deoxygenated via nitrogen bubbling. The Ag/AgCl
223 reference electrode was calibrated using a ferrocene/ferrocenium (Fc/Fc^+) redox couple as an
224 external standard. The HOMO energy was calculated from the voltammograms by taking the
225 mean value between the oxidation and reduction peak. Energies were converted such that the
226 vacuum served as reference, by subtracting 4.398 eV from the values where Ag/AgCl served
227 as the reference (See Electronic Supplementary Information S.3).

228 **2.5 Quantum chemical studies**

229 Electronic structure calculations were performed on parent dyes **1-4** and their computationally
230 engineered derivatives. These studies include DFT and TD-DFT calculations carried out using
231 *Gaussian 09*²⁹, and *ab-initio* equation-of-motion coupled-cluster methods (EOM-CC)³⁰,
232 using *Molpro*³¹, which feature the EOM-CC singles and doubles approximation (EOM-
233 CCSD)³² and the local coupled-cluster response method (LT-DF-LCC2).^{33,34}

234 The molecular structures of parent dyes **1-4**, obtained from single crystal X-ray diffraction,
235 were used as the input geometries for the calculations, which were geometrically optimized
236 using the hybrid functional of Perdew, Burke, and Ernzerhof (PBE0)³⁵⁻³⁸ with the 6-31G(p)
237 basis set.³⁹ Solvent effects were treated via the polarizable continuum model (PCM)^{40, 41} in
238 methanol. The iodide counter-ion was excluded from calculations since its presence did not
239 affect the geometry, nor the energies, of the molecule (See Electronic Supplementary
240 Information S.4.1 for full details). Vibrational frequencies were calculated for **1-4** and were all
241 found to be positive, indicating that reliable ground-state structures were found.

242

243 Single-point DFT energy calculations were performed on the optimized geometries in
244 order to determine HOMO energies and molecular-orbital spatial distributions. These
245 calculations were performed at the PBE0/6-311+G(2d,p) level of theory⁴² in methanol using
246 the PCM model. Orbitals were processed using cubgen²⁹ and visualized in *Avogadro*⁴³ at an
247 isovalue of 0.02. Difference-density plots between the squares of the HOMO and LUMO plots
248 were generated at an isovalue of 0.0007.

249 Excited state calculations were performed on the DFT-optimized geometry using the
250 Laplace-transformed local CC2 coupled cluster approximation with density fitting and a
251 double-zeta basis set (cc-pVDZ), with extended domains to account for the long-range
252 behaviour of D- π -A dyes. This computational method was selected after extensive
253 benchmarking of CC and TD-DFT methods, in order to establish an appropriate level of
254 theory (see Electronic Supplementary Information S.4.2 for full benchmarking details). The
255 benchmarks included the local functional B3LYP and functionals with long-range correction:
256 CAM-B3LYP and M06-HF, which overestimated excitation energies, compared to

257 experiments and CC methods. In light of the results of the benchmarks, lowest-vertical
258 excitation energies were calculated using LT-DF-LCC2, including solvent-shift effects.

259 **3 Results and Discussion**

260 **3.1 Establishing prerequisites to design optimal dyes**

261 The efficient molecular design of dyes for applications in DSCs requires a rational strategy.
262 The first step of this strategy involves an in-depth study of the structure and opto-electronic
263 properties of the parent dyes, **1-4**, from which DSC-functional chemical derivatives will be
264 computationally engineered. This study on **1-4** consists of a synergistic combination of
265 theoretical calculations and experiments. The chemical parameters to be investigated are the
266 molecular structure, energy levels and intra-molecular charge transfer pathways of each dye.
267 These chemical attributes can provide an understanding of the molecular origins of the
268 chemical and optical dye characteristics. Identifying the key functional fragments of **1-4**
269 involved in light absorption provides information about molecular modifications that might
270 enhance the electron injection from the dye to the TiO₂.⁴⁴ The low-lying vertical excitation
271 energies, E_V , are also investigated in the first part of this molecular engineering study. The
272 information gathered on the parent dyes is then used to design their molecular modifications.
273 The benchmarking of calculations on **1-4** against their associated experimental data ensures
274 that this information on the parent dyes emanates from reliable computational methods. This
275 experimental validation provides confidence in the further application of these methods to this
276 chemical family of dyes, via *in silico* computational re-engineering of these dyes, in order to
277 create DSC-functional chromophores. Figure 2 illustrates the results for parent dye, **1**, in terms

278 of this synergy between computation and experiment; associated data for **2-4** are available in
 279 the Electronic Supplementary Information, S.1-3 .

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Compound	E_v^{exptal} [eV] ($\lambda_{\text{max}}^{\text{peak}}$ [nm])	E_v^{calc} [eV]	ϵ [$\times 10^4$ L mol ⁻¹ cm ²]]	Λ [%]	HOMO ^{exptal} [eV]	HOMO ^{calc} [eV]	$E_{\text{ads}}^{\text{calc}}$ [eV]
1	2.57 ± 0.1 (482 ± 1)	2.62	9.9 ± 0.6	69	-5.30 ± 0.02	-5.93	-1.87
2	2.23 ± 0.1 (555 ± 1)	2.41	6.4 ± 0.2	70	-5.45 ± 0.02	-5.83	-1.86
3	1.90 ± 0.1 (652 ± 1)	2.02	10.8 ± 0.2	71	-5.43 ± 0.02	-5.59	-1.84
4	1.64 ± 0.1 (756 ± 1)	1.72	11.0 ± 1.2	70	-5.36 ± 0.02	-5.41	-1.54

284

285 Table 1: Optical absorption characteristics, including vertical excitation energies (E_v), HOMO
 286 energies, molecular orbital overlaps (Λ) and dye adsorption energies for **1-4**. All measurements were
 287 performed in methanol. The experimental vertical excitation energies, E_v^{exptal} , were estimated by the
 288 maximum absorption wavelength, $\lambda_{\text{max}}^{\text{peak}}$. Calculated E_v^{calc} values were determined using LT-DF-
 289 LCC2. Adsorption energies were calculated assuming a carboxylic acid anchoring group at the para-
 290 quinoidal position in **1-4**.

291 **3.1.1 Molecular dye architecture and intra-molecular charge transfer of 1-4**

292 The bond geometry from the crystal structures of the parent dyes **1**, **2** and **4** (see Electronic
293 Supplementary Deposition Material) and DFT optimized structures of **1-4** were used to reveal
294 properties about the intra-molecular charge transfer characteristics.

295 With the exception of **4**, the dye molecules exhibit rotational symmetry with a C_2 axis
296 situated in the center of the molecule, perpendicular to the plane of the polymethine chain.
297 The presence of ethyl groups prevents higher point group symmetries. The structure of **4** has
298 mirror symmetry C_s , with the mirror plane lying normal to the polymethine chain. Given the
299 nature of these symmetries, **1-4** have two donor units, which are situated on the nitrogen
300 atoms. The central polymethine chain represents the π -conjugated fragment contributing to the
301 optical absorption.¹⁹ Analysis of the bond-length alternation (BLA), defined as the difference
302 between the average carbon-carbon single and double bond lengths^{45, 46}, shows that the
303 atomic separations in the polymethine chain differ by a maximum of 0.005 Å. C-N bond
304 lengths vary between 1.347(4) and 1.359(6) Å, indicating a reduction in double bond character
305⁴⁷, i.e. the lack of a definite resonance structure. The same observation holds for the DFT
306 optimized structures. This concept is reinforced by a low bond-length alternation in the
307 polymethine chain, suggesting π -conjugated electron density, which diffuses over the entire
308 length of the chain, making its extent of delocalization close to the "cyanine limit".⁴⁸

309 These structure indicators were backed up by further analysis of bond geometries from the
310 crystal structures using harmonic oscillator stabilization energies (HOSE) to determine the
311 prevalent resonance structure.^{49, 50} HOSE is a measure of the energy needed to transform the
312 idealized bond geometry of a particular resonance structure to the geometry of a real
313 molecule.⁵¹ It is defined as

314
$$HOSE_j = \frac{1}{2} (\sum_{r=1}^{n_1} (R'_r - R'_o)^2 k'_r + \sum_{r=1}^{n_2} (R''_r - R''_o)^2 k''_r) \quad (1)$$

315 for each resonance structure, j , where: $k_r = a + bR_r$ are the force constants; R'_r and R''_r are,
 316 respectively, the measured single and double bonds; R'_o and R''_o are single and double bonds
 317 from reference values. a and b are empirical constants, measured as: $a = 44.39 \times 10^4$ Pa, $b = -$
 318 26.02×10^4 Pa, while $R'_o = 1.467$ Å and $R''_o = 1.349$ Å. The HOSE model can be used to
 319 compute the relative contributions of each canonical resonance structure to that of the real
 320 molecule. These contributions, C_i , are calculated according to:

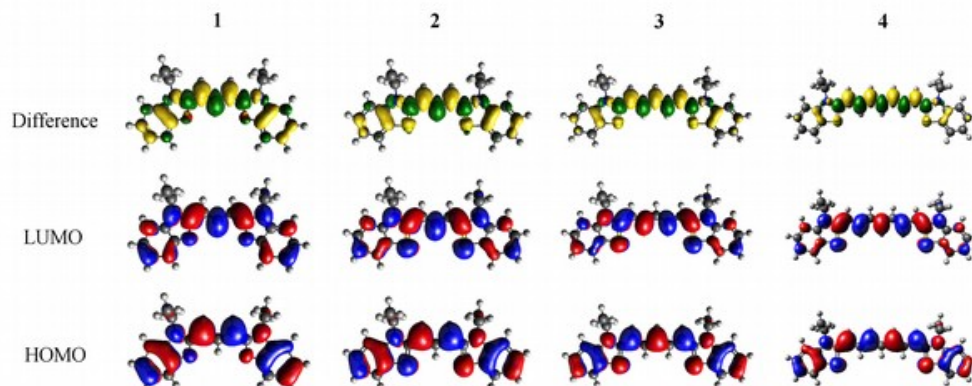
321
$$C_i = \frac{(HOSE_i)^{-1}}{\sum_{j=1}^N (HOSE_j)^{-1}} \quad (2)$$

322 Since C_i is inversely related to the HOSE value, an energetically more stable structure (lower
 323 energy) will result in a larger contribution, C_i . Only two Kekulé canonical structures are
 324 possible for **1-4**. For both arene rings in each compound, the HOSE analysis shows a
 325 contribution of ca. 50% for each of the two possible Kekulé structures, with deviations from
 326 these figures up to 10%. This reflects an electronically delocalized polymethine chain, since a
 327 larger contribution of any of the two Kekulé canonical structures would have implied a
 328 preferred resonance structure, with a definite bond-length alternation and a positive charge
 329 deposition on one of the two nitrogens.

330 Density functional theory calculations on **1-4** provided complementary insight into the
 331 extent of the intra-molecular charge transfer and its possible bond pathways. In particular,
 332 visualizing the computed frontier orbitals enabled the regions of the molecule with greater
 333 electron density to be identified. HOMO and LUMO orbitals for **1-4** are depicted in Figure 5.
 334 Given that these E_V values pertain to HOMO→LUMO transitions, they represent the change

335 in electron density from the ground state to the excited state. Corresponding difference orbital
336 plots, calculated as $LUMO^2 - HOMO^2$, highlight areas of electron density withdrawal and
337 donation during the optical excitation process. The overall extent of intra-molecular charge
338 transfer was enumerated via the orbital overlap measure (Λ)⁵², which quantifies the amount of
339 orbital overlap between HOMO and LUMO orbitals across the dye molecule. As is evident
340 from the orbital plots, there is a high degree of spatial overlap between the HOMO and
341 LUMO orbitals, amounting to $69\% < \Lambda < 71\%$. Values of Λ for **1-4** are reported in Table 1.

342



343
344

345 Figure 5: HOMO and LUMO Kohn-Sham orbitals of the parent dyes **1-4**, generated from
346 DFT calculations at the PBE0 level of theory with 6-311+G(2d,p) basis set and PCM.
347 Corresponding difference density orbitals are also generated by subtracting the square of the
348 LUMO orbitals from the square of the HOMO orbitals. Increasing electron density is
349 represented in green, while decreasing electron density is represented in yellow. Orbitals have
350 been drawn at an isovalue of 0.02 for HOMO and LUMO orbitals, and at an isovalue of
351 0.0007 for the difference orbitals.

352 **3.1.2 Optical characteristics of the parent dyes, 1-4**

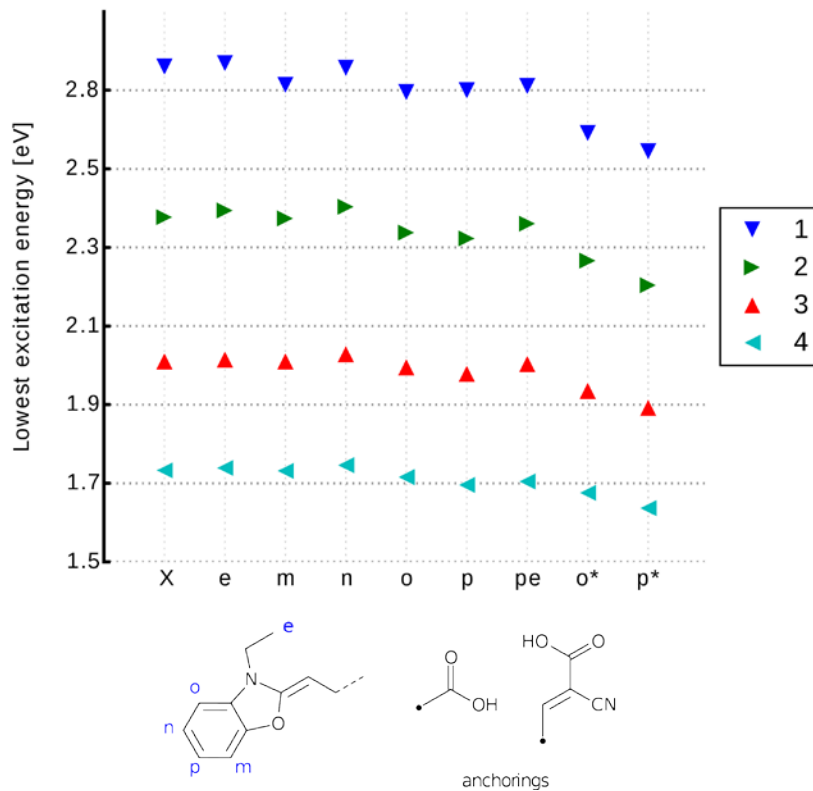
353 UV/vis absorption spectroscopy determined the optical absorption profiles of **1-4**, measured in
354 methanol at a concentration of 0.01 mM (Figure 4). The wavebands of these spectral profiles
355 are complementary in that, when taken together, certain combinations of parent dyes can yield
356 near-panchromatic optical absorption. Differences in the maximum peak absorption
357 wavelength (ca. 75 nm) between **1** and **2** are the result of the substitution of an oxygen atom
358 for a sulfur atom in the heterocycles. Differences of approximately 95 nm (between **2** and **3**)
359 and 105 nm (between **3** and **4**) are observed by extending the central polymethine chain by
360 one vinylene unit. This structure-function relationship has been observed previously in
361 cyanine dyes ¹⁹, and renders them an optically tunable class of chromophore. The lowest-
362 excitation energy for each dye molecule can be estimated experimentally as corresponding to
363 the intersection of the two superimposed curves of a UV/vis absorption spectrum 1; results are
364 reported in Table 1.

365 Molar extinction coefficients, ϵ , were also measured for all parent dyes (Table 1) which
366 showed no sign of molecular aggregation in methanol, as judged by their correspondence with

367 the Beer-Lambert law, in the context of relating changes in optical absorbance to variation in
368 dye concentration. This is in spite of the fact that cyanines have been long known to form
369 aggregates.^{19, 53}

370 Computational calculations, using LT-DF-LCC2 with solvent correction, complemented
371 these experimental results. Calculated and experimental lowest-excitation energies, E_V ,
372 differed by 0.12 eV (Table 1). The implicit inclusion of solvent in all computed models was
373 deemed mandatory (see Electronic Supplementary Information S.4.2).

374



375

376 Figure 6: LT-DF-LCC2 calculated lowest-excitation energy for derivatives of **1-4** engineered
377 with an anchoring group at different positions. **X** refers to the parent dye; **e** (ethylene), **m**
378 (meta-1), **n** (meta-2), **o** (ortho), **p** (para) involve addition of the carboxylic acid anchoring
379 group (COOH) at the indicated positions. **pe** involves the addition of COOH at both **p** and **e**
380 positions. **o*** and **p*** are respectively the ortho- and para- substitutions of cyanoacrylic acid as
381 anchoring group.

382 **3.2 Molecular engineering DSC dyes**

383 **3.2.1 Design strategy for adding an anchoring group**

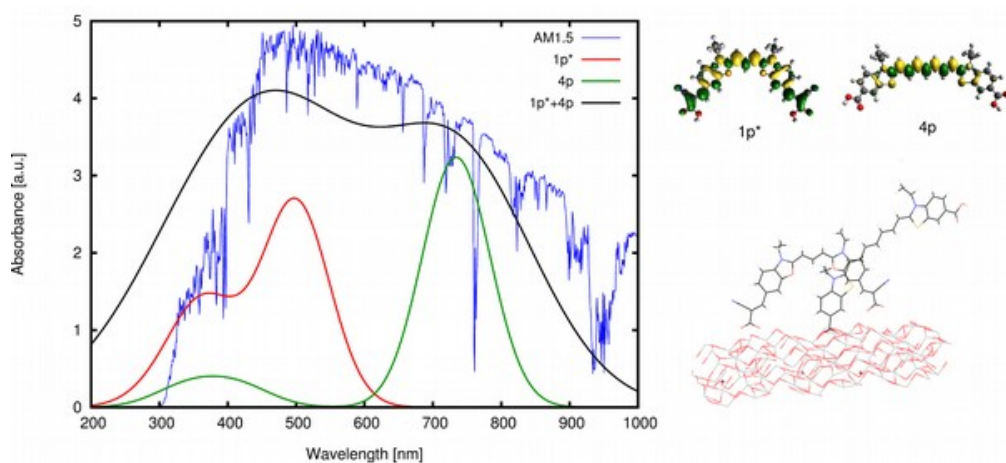
384 The findings from this prerequisite study on **1-4** (§ 3.1) are useful to set a constraint on
385 possible molecular modifications of this family of dyes to functionalize them for DSC
386 applications. To this end, they feed into the molecular design strategy for adding an anchoring
387 group as follows: (i) The analysis of the frontier orbital shapes can suggest the best chemical
388 substitution point to attach the anchoring group, such as the molecular region of the dye which
389 is associated with its LUMO orbital weighting.⁴⁴ (ii) Determining a suitable substitution point
390 to add an anchoring group to a parent dye is also aided by identifying the nature of its D- π -A
391 molecular architecture, which has, in turn, been determined by bond geometry analysis of the
392 structures of **1-4** within this study. (iii) The anchoring unit must be added to a dye at a position
393 which allows the molecule to easily attach to the TiO₂ surface. The prerequisite studies on **1-4**
394 can identify steric effects from molecular fragments that could physically hinder dye···TiO₂
395 adsorption. A dye that bears a D- π -A structure such that the donor is further away from the
396 TiO₂ surface upon adsorption, while the π -conjugation and acceptor moieties reside close to

397 the anchoring group, is preferred in order to prevent electronic losses from recombination with
398 the electrolyte.

399 The ICT pathways in **1-4** span the entire molecule, excluding the ethyl units since they
400 lack π -conjugation to be able to transfer charge. This makes the ethyl groups an unsuitable
401 place for adding an anchoring group. The difference density molecular orbital plots for **1-4**
402 (Figure 5) do not obviously suggest a favorable position for the anchoring group. On the one
403 hand, an excess of electron density in the polymethine chain could suggest helpful chemical
404 substitution along the chain; on the other hand, adding a carboxyl group at this point would
405 impede successful dye··TiO₂ anchoring because of steric hindrance. In contrast, the arene
406 rings are sterically and electronically favorable fragments for an anchoring group. On each
407 ring, there are two meta-, one para- and one ortho- possible substitution positions.

408 The chemical nature of the anchoring group is similarly important to that of its substitution
409 position. Despite the plethora of research that details the effects of different anchoring groups
410 on DSC performance⁵⁴, it has been hard to find the best anchoring group for any given DSC.
411 This difficulty stems from the largely diverse effect of dye··TiO₂ anchoring on its different
412 molecular environments, where there is a large variety of dye molecules and electrolyte redox
413 couples.⁵⁴ To date, the primal carboxylic acid group, -COOH, has been the most used and
414 reliable anchoring group. For this reason, it will be used in this study. The computational
415 substitution of a chemically related, but larger, type of anchoring group, a cyanoacrylic acid⁵⁴,
416 was also performed. Here, the points of substitution explored were pre-selected, choosing only
417 the points of dye attachment which showed promise when anchor addition involved the -
418 COOH group.

419 Given the nature of this molecular-design exploration of the anchoring group type and
420 point of substitution in **1-4**, a set of chemical derivatives was tailored for optical function
421 using DFT, TD-DFT and LT-DF-LCC2 methods. These molecularly-engineered dyes were
422 named as follows. Parent dyes (**X=1-4**): **X**; carboxylic acid substitutions at the two meta-
423 positions relative to the N donor: **Xm** and **Xn**; at the corresponding ortho- position: **Xo**; at the
424 para- position: **Xp**; on the ethyl units: **Xe**; double anchoring at the para- position and on the
425 ethyl moieties (as reported by Ehret et al. ⁵⁵): **Xpe**; for cyanoacrylic acid at the ortho- position:
426 **Xo*** and cyanoacrylic acid at the para- position: **Xp***. Figure 6 provides a chemical schematic
427 of these substituted dye molecules.



428
429

430 Figure 7: (Left) Calculated absorption spectra of the selected dyes for co-sensitization, **1p***,
431 and **4p**, along with their superposition and the solar emission spectrum at AM1.5. The
432 absorption spectra are calculated by convoluting a Gaussian window function to the excitation
433 energies, weighted by the oscillator frequencies. The excitation energies were calculated at the
434 M06-HF level of theory (after a benchmark of different functionals) and shifted in order to
435 match the lowest-excitation energy with the one calculated using LT-DF-LCC2. The
436 superposed absorption spectrum of **1p*** and **4p** was calculated by convoluting a Gaussian
437 window function with a larger full width at half maximum than the convoluted Gaussian
438 function for single dyes, in order to visualize the broadening of the absorption spectrum for
439 adsorbed dyes. (Right-Top) Difference molecular orbitals of the selected dyes. (Right-Bottom)
440 Simulated adsorption modes for both dyes on a non-optimized slab of TiO₂ particles (§ 3.3).

441 3.2.2 Determining a suitable pair of dyes for co-sensitization in DSCs

442 The aim of computationally generating a series of chemical derivatives of **1-4**, which bear
443 anchoring groups at a range of possible substitution points, is to find a matching pair of dyes
444 which synergistically contribute to broadening the optical absorption spectrum. This is
445 achievable by using dyes which exhibit complementary optical absorption spectra, whereby
446 their combined $\lambda_{\text{max}}^{\text{peak}}$ values result in panchromatic optical absorption. Chemical substitution
447 of a parent dye that affords an energy shift that widens the difference between $\lambda_{\text{max}}^{\text{peak}}$ values
448 of two complementary dyes are favorable, up to the point where the optical gap between
449 spectral profiles of each dye compromise optical absorption in the middle region.

450 3.2.2.1 Adding an anchoring group

451 Visual inspection of the molecular geometry imposed by attaching either type of anchoring
452 group at the ortho- position, **Xo** and **Xo***, as defined in Figure 6, shows that the process of
453 anchoring the dye on the TiO₂ would be prevented by substantial steric hindrance from the
454 ethyl units. Nonetheless, single-point DFT energy calculations indicated that ortho- and para-
455 positions are the most effective substitution points for the primal carboxylic acid attachment,
456 given this substitution afforded increased electron density at this anchoring point for each of
457 the parent dyes. An even stronger trend is observed where cyanoacrylic acid is employed as
458 the anchoring moiety. Although unsuitable for a DSC device, attaching an anchoring group at
459 the ortho- position shows the largest increase in electron density around this point of
460 substitution. This is quantified by analyzing the Tozer index for spatial orbital overlap. For
461 **1o***, Λ drops to 54% from a value of 69% for the parent dye, **1**. By comparison, the
462 corresponding para- substitution option for cyanoacrylic acid, **1p***, affords an orbital spatial
463 overlap, Λ , of 62% and associated -COOH derivatives of **1** oscillate from 66% to 69%. Less
464 variation is observed in parallel calculations featuring the other parent dye frameworks **2-4**,
465 with **4** showing the smallest variation. Derivatives **4o*** and **4p*** have, respectively, Tozer
466 indices of 66% and 68% (see Electronic Supplementary Information S.4.3). This trend is
467 reflected in the difference orbital plots (see Electronic Supplementary Information S.4.3) and
468 replicated in the context of the lowest-excitation energies.

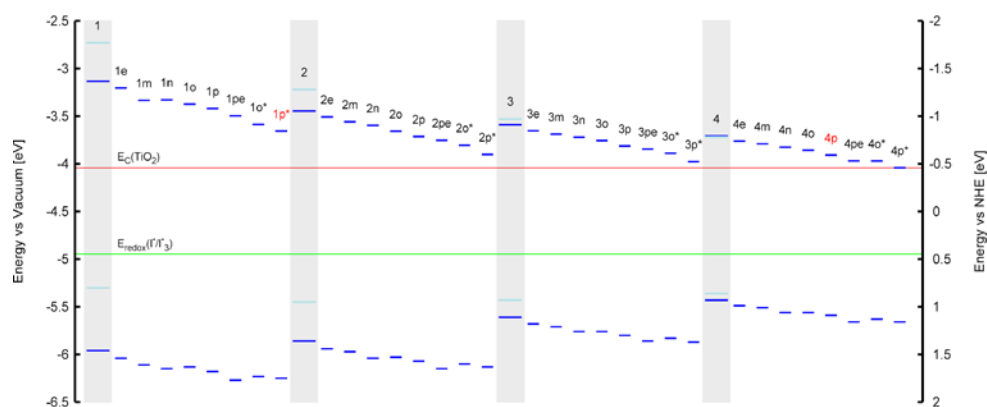
469 These lowest-excitation energies were analyzed for all derivatives using LT-DF-LCC2
470 calculations. By analyzing the shifts in peak maximum optical absorption wavelengths,
471 $\Delta\lambda_{\text{max}}^{\text{peak}}$, achieved upon anchoring group addition, a bathochromic shift was observed in all
472 cases, except for those where the anchor was added to the ethyl group (**Xe**). This can be

473 rationalized by noting that the substitutions are, by prior design, targeted on regions with high
474 electron density. The addition of an electron withdrawing unit onto high electron density
475 regions, such as the subject anchoring options, stabilizes each dye, lowering its excitation
476 energy.⁵⁶ Substituents on the ethyl groups do not lie in the ICT pathway and so cause small
477 changes in excitation energy, which manifest in the hypsochromic direction; this can be
478 explained by their proximity to the donor part of the molecule. For all dyes, the addition of a
479 primal carboxylic acid at the meta- positions, **Xm** or **Xn**, or on the ethyl groups, **Xe**, did not
480 cause a significant energy shift in lowest-excitation energy. Furthermore, the associated
481 derivatives do not allow charge transfer from the donor moiety, and so they will not be
482 considered for co-sensitization. The difference in energy between ortho- and para- positions
483 for the -COOH substitution is negligible. Considering the aforementioned negative steric
484 effects of ortho- substitutions, only para- substitutions will be taken forward for co-
485 sensitization.

486 With para- substitution in mind, it is possible to fine tune the choice of dye and anchoring
487 group by considering the structure and energetic requirements of a DSC device in terms of
488 achieving optimum dye...TiO₂ adsorption characteristics for enabling electron injection, and
489 realizing panchromatic optical absorption via co-sensitization. Visual inspection of the
490 molecular geometry of **1p*** shows that its anchoring groups lie perpendicular to the long π -
491 conjugated axis of the molecule. This structure allows for double-anchoring onto the TiO₂
492 surface. All other *in silico* generated derivatives of **1-4** display anchoring groups at a larger
493 dihedral angle than 90°; as such, they can only be attached to the TiO₂ by one of the two
494 anchors.

495 The co-sensitization of **1p*** with one of the singly-anchored dyes would remove any
 496 possibility of dye aggregation that would be detrimental to device functioning due to $\pi \cdots \pi$
 497 stacking between dye molecules. Consulting the computed optical absorption spectra of each
 498 chemical derivative of **1-4**, an optimal dye candidate for co-sensitizing with **1p*** appears to be
 499 **4p**. The $\lambda^{\text{peak}}_{\text{max}}$ of **4p** is the farthest from the corresponding maximum absorption wavelength
 500 of **1p***, providing an absorption spectrum that extends across UV, visible and near-IR
 501 wavelengths when **1p*** and **4p** are combined via co-sensitization. Their computed absorption
 502 profiles present an excellent panchromatic match to that of the solar absorption spectrum, as
 503 simulated in Figure 7. Furthermore, the presence of both types of anchoring groups explored
 504 for these dyes would perhaps be advantageous, as they can occupy different TiO_2 adsorption
 505 sites, possibly preventing dye competition upon their sensitization onto TiO_2 .⁵⁷ The orbital
 506 energy levels of **1p*** and **4p**, relative to those of the other material components of a DSC
 507 device, were also found to be suitable: as shown in Figure 8, their HOMOs and LUMOs are
 508 lower and higher in energy, respectively, than that of the electrolyte or conduction-band edge
 509 of TiO_2 .

510



511

512 Figure 8: HOMO and LUMO energies for **1-4** and chemical derivatives where an anchoring
513 group has been added. HOMO energies are all below the electrolyte reduction potential, while
514 LUMO energies are all above the TiO₂ conduction band. The identified co-sensitizers pairing,
515 **1p*** and **4p**, are highlighted in red. Experimental values are represented in light blue, while
516 calculated values are displayed in dark blue. Calculated LUMO energies are found by adding
517 the lowest-vertical excitation energy (calculated using LT-DF-LCC2) to the HOMO energy.
518 Experimental HOMO energies are found using cyclic voltammetry. Experimental LUMO
519 energies are found by adding the lowest-vertical excitation energy (measured using UV/vis
520 absorption spectroscopy) to the experimental HOMO energy. The TiO₂ conduction band and
521 electrolyte reduction potential are represented by two horizontal lines in red and green colors,
522 respectively.

523 3.2.2.2 Tuning the polymethine chain length

524 The length of the polymethine chain is well known to produce changes in peak optical
525 absorption wavelengths, $\lambda_{\text{max}}^{\text{peak}}$.⁵⁸ Cyanine dyes are likely to be particularly susceptible to
526 this structure-property relationship, owing to their unusually high levels of electron
527 delocalization within their π -conjugated chains cf. the "cyanine limit".⁴⁸ Accordingly, the
528 effect of progressively adding vinylene groups (up to 8 in total) to the π -conjugated chain on
529 the $\lambda_{\text{max}}^{\text{peak}}$ of **1-4** was explored. Given that **1** contains oxygen and two vinylene groups while
530 **2-4** contain sulfur and two, three or four vinylene units, respectively, computationally-
531 generated dyes with polymethine chains containing n-vinylene variations were named as **o3**,
532 **o4**, **o5**, **o6**, **o7**, **o8** for π -conjugated extensions of **1**, and **s5**, **s6**, **s7**, **s8** for extensions of **2-4**.

533 This study involved the same model and functional employed in the computation of the
534 anchoring group substitutions. Visual inspection of the resulting molecular structures shows
535 that ICT pathways were not modified by increasing the extent of π -conjugation. Their HOMO
536 and LUMO orbitals have similar shapes for all derivatives and the only difference is found in
537 the extended electron densities on the polymethine chain. A lengthened chain has a larger
538 amount of electron density. This result did not seem to affect the amount of spatial overlap
539 that is shared by the HOMO and LUMO orbitals. Tozer indices for all derivatives were stable
540 at around 70%. An associated HOSE analysis did not reveal a significant bias towards one of
541 the two possible Kekulé resonant structures for any of the derivatives; this suggests that an
542 energy-stabilized state exists irrespective of the polymethine chain length.

543 A clear relationship was observed, however, between the extent of molecular planarity of
544 the sulfur-containing dyes (**2-4** and **s5-s8**) and the polymethine chain length. Table 2
545 evidences a subtle, nonetheless consistent, monotonic decrease in the torsion angle between
546 the arene rings in **2-4** and **s5-s8** as a function of increasing polymethine chain length. This
547 suggests an increase in the extent of molecular planarity for longer polymethine chains. The
548 rate of change was best fitted by a cubic polynomial. Such a rational relationship was not
549 replicated in the oxygen-based dyes, **1** and **o3-o8**. Nonetheless, the corresponding E_V values
550 show a consistent reduction with increasing π -conjugated chain length in O- and S-containing
551 dyes. In all cases, HOMO and LUMO energies lie within the energy bounds associated with
552 those of the other salient DSC device components (see Figure 9). Thus, they are eminently
553 adaptable to DSC applications. The trend towards lower E_V values with increasing
554 polymethine chain length means that a more panchromatic range of optical absorption

555 energies is realized for dyes with longer π -conjugated units, while a corresponding energy
556 shift in E_V towards the NIR region of the absorption spectrum is also achieved.

557 That said, a trade-off is observed between dyes with longer π -conjugated polymethine
558 units and progressively NIR absorption wavelengths. As shown in Figure 9, the LUMO and
559 HOMO levels tend increasingly towards the TiO₂ conduction band energy level and the
560 electrolyte redox potential energy levels, respectively, as the polymethine chain lengthens.
561 Detrimental reduction in driving forces for electron injection and dye regeneration may result.
562 Therefore, since a sufficient panchromatic range was afforded by the **1p*** and **4p** co-
563 sensitizers identified in the previous section, the polymethine chain length was not extended to
564 avoid this compromising trade-off. Nonetheless, the generic findings of this trade-off effect
565 are helpful to observe in the context of further molecular design studies of cyanine-based DSC
566 dyes.

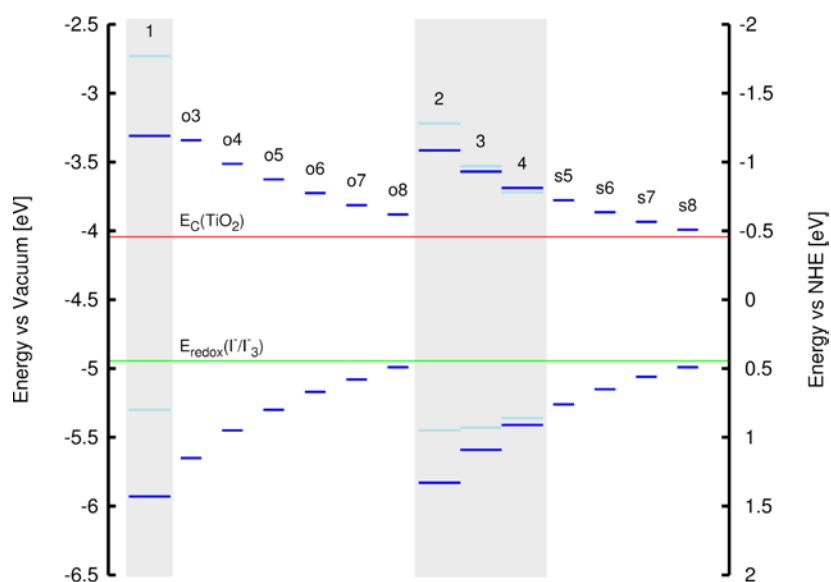
567

Vinylene units	E_V (O) [eV]	E_V (S) [eV]	Torsion angle (S) [°]
2	2.62	2.41	4.42
3	2.31	2.02	3.47
4	1.94	1.72	2.77
5	1.67	1.48	2.40
6	1.44	1.28	2.22
7	1.27	1.13	2.13
8	1.11	1.00	2.10

568

569 Table 2: Calculated lowest-vertical excitation energies and torsion angles for cyanine
570 derivatives with modifications on the central polymethine chain. The parent dye, **1**, contains
571 an oxygen in each of the two heterocycle rings and two vinylene units. Parent dyes, **2-4**,
572 contain a sulfur in each of the two heterocycle rings and two, three or four vinylene units,
573 respectively.

574



575

576 Figure 9: HOMO and LUMO energies for **1-4** and chemical derivatives, where the length of
577 the polymethine chain has been modified. HOMO energies are all below the electrolyte
578 reduction potential, while LUMO energies are all above the TiO₂ conduction band.
579 Experimental values are represented in light blue, while calculated values are displayed in
580 dark blue. Calculated LUMO energies are found by adding the lowest-vertical excitation
581 energy (calculated using LT-DF-LCC2) to the HOMO energy. Experimental HOMO energies
582 are found using cyclic voltammetry. Experimental LUMO energies are found by adding the
583 lowest-vertical excitation energy (measured using UV/vis absorption spectroscopy) to the
584 experimental HOMO energy. The TiO₂ conduction band and electrolyte reduction potential
585 are represented by two horizontal lines in red and green colors, respectively.

586 **3.3 Modeling the Dye···TiO₂ interface**

587 While computational modeling of isolated dyes in a gas or solution medium provides a rapid
588 and accurate description of their opto-electronic properties, the dynamics of the dye at the
589 dye···TiO₂ interface may differ. Indeed, examples exist where the process of anchoring the
590 dye onto the TiO₂ changes the geometry and the energies of the molecular chromophore.^{59, 54,}
591 ⁶⁰ Furthermore, the anchoring process may be energetically unfavorable for certain dye···TiO₂
592 combinations, making dye adsorption difficult to achieve. More advanced computational
593 methods that model the dye···TiO₂ interface, via various binding modes, were therefore
594 applied to a small selection of the more promising computationally designed dyes, **1p**, **2p**, **3p**
595 and **4p**, as judged by the aforementioned gas and solution-phase dye studies (§3.1 and §3.2).

596 These advanced methods employed DFT and TD-DFT using a (TiO₂)₉ cluster
597 predetermined by Sanchez de Armas et al.⁶¹ (see Electronic Supplementary Information

598 S.4.4). Its binding to the dye was modeled by considering the three most common possible
599 types of anchoring modes for a carboxylic acid: monodentate, bidentate chelating and
600 bidentate bridging. Dyes bearing the primal carboxylic acid anchoring group were selected for
601 the initial stage of this advanced modeling rather than the cyanoacrylic acid because its
602 smaller molecular fragment size eases computational cost. Previous studies have shown that
603 (TiO₂)₉ clusters are of a sufficient size that they present a good compromise between
604 providing an accurate representation of the TiO₂ surface and computational cost.⁶²⁻⁶⁴ The
605 geometry of each dye···TiO₂ interface was optimized using DFT at the B3LYP level of theory
606 and 6-31G* basis set in ethanol (PCM). Single-point energy calculations and excitation
607 energies were calculated using DFT and TD-DFT, respectively, at the B3LYP level of theory
608 and 6-311+G* basis set in ethanol (PCM).

609 The exploration of the three possible anchoring modes on **1p** revealed that the HOMO, E_v
610 and atomic orbital energies were invariant with anchoring mode. Differences between these
611 modes were evident, however, in the associated adsorption energies which were calculated
612 according to the formula:

$$613 \quad E_{ads} = E_{dye} + E_{TiO_2} - E_{dye/TiO_2} \quad (3)$$

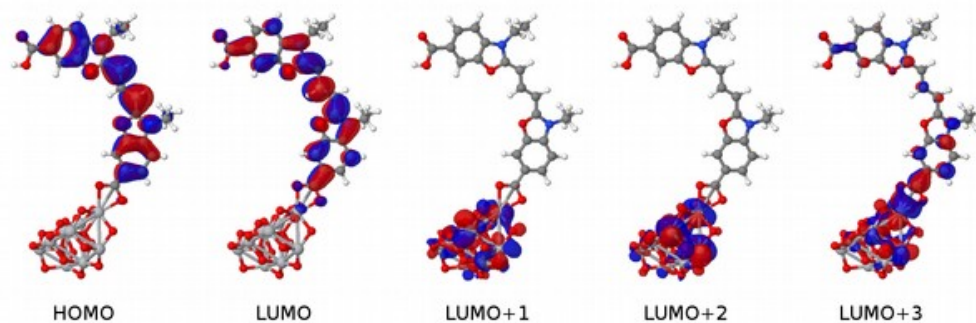
614 where E is the single-point DFT energy calculation for the different anchoring dye···TiO₂
615 configurations.⁶⁵ The monodentate adsorption energy was -1.47 eV, while that of bidentate
616 bridging was -0.84 eV and bidentate chelating was -1.87 eV. The negative values of
617 adsorption energies show a successful reduction in energy upon dye···TiO₂ adsorption,
618 making the bidentate chelating mode the most energetically favorable structure.

619 The dye...TiO₂ models that employ the bidentate chelating mode of **1p**, **2p**, **3p** and **4p**
620 onto TiO₂ were then computed and compared with those of their respective **1p**, **2p**, **3p** and **4p**
621 dyes in solution. HOMO energies were 0.1-0.2 eV higher for the dyes in solution, while the
622 vertical excitation energies were equivalent. The HOMO→LUMO transition, involved in E_v,
623 shows some increased electron density on the anchoring group, similar to the behavior in
624 solution. A study of non-frontier energetic transitions shows that there are changes between
625 the dye at the dye...TiO₂ interface and when in solution. These were assigned to higher
626 electronic transitions such as HOMO→LUMO+1, HOMO→LUMO+2 and
627 HOMO→LUMO+3. Visual inspection of the orbital plots shows that these higher-order
628 transitions involve both orbitals of the dye and the TiO₂, as depicted in Figure 10. This plot
629 also shows that the electron density progressively shifts from the dye to the semiconductor as
630 a function of increasing optical absorption energy, as denoted by the changing molecular
631 orbital population trends from HOMO to LUMO+3. This suggests that the electron injection
632 required to initiate the electrical current in a DSC is eminently viable. Whilst all dyes show
633 similar trends in the atomic orbitals, the adsorption energies varied between dyes by up to 0.3
634 eV (Table 1). Based on these considerations, the most suitable para-substituted COOH-
635 bearing dye for anchoring proved to be **1p**, which proceeds via bidentate chelating bearing an
636 adsorption energy of -1.87 eV.

637 The dye...TiO₂ model for the dye derivatives earlier selected for co-sensitization, **4p** and
638 **1p***, was then computed employing the bidentate chelating mode. Lowest-vertical excitation
639 energies and HOMO energies were equivalent to the isolated dye in solution medium and the
640 molecular orbitals involved in the transition were HOMO→LUMO, as for **1p-3p**. Orbital
641 plots showed a similar trend as the one depicted in Figure 10, indicating the viability of

642 electron injection for these dyes. Adsorption energies for **4p** and **1p*** were -1.54 eV and -1.71
643 eV, respectively, indicating a favorable and stable adsorption of the dyes onto the TiO₂. This
644 computational study of the dye-TiO₂ interface for **4p** and **1p*** therefore corroborated the
645 suitability of these dyes for application in a co-sensitized DSC.

646



648 Figure 10: Molecular orbitals of **1p** attached to a slab of (TiO₂)₉, involved in electronic
649 transitions upon photoexcitation. Excited states show a deposition of charge on the TiO₂
650 cluster, which hints at a successful electron injection. Plots for **1p***, **2p**, **3p**, **4p** are essentially
651 equivalent to **1p**.

652 **4 Conclusions**

653 Four cyanine dyes **1-4** have been studied experimentally and computationally, and
654 subsequently re-engineered using calculations that are designed to functionalize their structure
655 and enhance their optical response for DSC applications. The study adopted a synergistic
656 combination of experimental and computational methods to first reveal the structure and opto-

657 electronic properties of the parent dyes. A molecular engineering strategy was then rationally
658 designed and performed on these parent cyanine dyes in order to make them suitable for use in
659 DSCs and broaden their absorption spectrum for co-sensitization. Two different types of
660 anchoring groups, the primal carboxylic acid and cyanoacrylic acid, were strategically tested
661 at different substitution positions on **1-4**. The effect of lengthening the central polymethine
662 chain was also explored and the dye...TiO₂ interface was analyzed via further *in silico*
663 calculations.

664 The central polymethine chain was extended up to 8 vinylene units. All modified dyes
665 showed successful features for applications in DSCs and absorption spectra reaching
666 wavelengths beyond the NIR region. The best reported chemical substitution points for both
667 anchoring types were found to be at the para- position. Dye...TiO₂ interface studies on four
668 derivatives with -COOH anchoring groups at the para- position showed successful adsorption
669 and charge injection onto a modeled (TiO₂)₉ cluster. Two of the molecularly-engineered dyes,
670 **1p*** and **4p**, were selected for co-sensitization on the basis of their suitability in a real DSC,
671 mitigation of unfavorable aggregation and complementarity of the absorption spectrum; their
672 simulated absorption spectra spanned UV, visible and NIR regions.

673 We have shown that molecular engineering provides a cheap and useful rational tool in
674 screening refunctionalized dye candidates and fine tuning their properties, through molecular
675 modifications, to achieve the best performing dye co-sensitized solar cell for a given class of
676 dyes. This is one of few examples of "bottom up" rational dye design⁶⁶, which complements
677 the "top down" approach associated with large-scale data mining for materials discovery of
678 new classes of dyes.⁶⁷ Such strategies allow one to move away from previous efforts where
679 new dyes have been found via trial-and-error, which is very costly and time consuming. This

680 systematic design concept is even more important when considering the recent interest in co-
681 sensitization techniques. Co-sensitization introduces additional molecular design factors that
682 leaves the possibility of finding a successful combination of dyes through blind search and
683 experiments to pure chance. Complications such as chemical compatibility, dye competition
684 and complementarity of the absorption spectrum arise in these types of DSCs. This study
685 shows that these problems can be efficiently and cheaply tackled through systematic design
686 and computational screening, which will become essential for future development of efficient
687 co-sensitized DSCs.

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689
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698 **References and Notes**

- 699 1 A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, *Chem. Rev.* , 2010, **110**, 6595.
700 2 Z. Xie, *et al.*, *Chem. Commun.* , 2014, **50**, 608.
701 3 C. Bechinger, S. Ferrere, A. Zaban, J. Sprague, B. A. Gregg, *Nature* , 1996, **383**, 608.
702 4 K.-S. Ahn, S. J. Yoo, M.-S. Kang, J.-W. Lee, Y.-E. Sung, *Journal of Power Sources* , 2007, **168**, 533.

703 5 B. O'Regan, M. Grätzel, *Nature*, 1991, **353**, 737.

704 6 A. Yella, *et al.*, *Science*, 2011, **334**, 629.

705 7 K. Kakiage, *et al.*, *Chem. Commun.*, 2015, **51**, 15894.

706 8 M. Kimura, H. Nomoto, N. Masaki, S. Mori, *Angew. Chem.*, 2012, **124**, 4447.

707 9 G. Boschloo, A. Hagfeldt, *Acc. Chem. Res.*, 2009, **42**, 1819.

708 10 G. D. Sharma, S. P. Singh, R. Kurchania, R. J. Ball, *RSC Advances*, 2013, **3**, 6036.

709 11 T. Bessho, S. M. Zakeeruddin, C.-Y. Yeh, E. W.-G. Diau, M. Grätzel, *Angew. Chem.*, 2010, **122**, 6796.

710 12 S. Maniam, *et al.*, *Org. Lett.*, 2015, **17**, 4022.

711 13 D. Pugliese, *et al.*, *Org. Electron.*, 2014, **12**, 3715.

712 14 G. D. Sharma, M. S. Roy, S. P. Singh, *J. Mater. Chem.*, 2012, **22**, 18788.

713 15 B.-G. Kim, K. Chung, J. Kim, *ChemInform*, 2013, **44**, no.

714 16 B. E. Hardin, H. J. Snaith, M. D. McGehee, *Nat. Photonics*, 2012, **6**, 162.

715 17 W. Wu, F. Meng, J. Li, X. Teng, J. Hua, *Synth. Met.*, 2009, **159**, 1028.

716 18 A. Burke, L. Schmidt-Mende, S. Ito, M. Graetzel, *ChemInform*, 2007, **38**.

717 19 A. Mishra, R. k. Behera, P. K. Behera, B. K. Mishra, G. B. Behera, *ChemInform*, 2000, **31**, no.

718 20 A. Ehret, L. Stuhl, M. T. Spitler, *J. Phys. Chem. B*, 2001, **105**, 9960–9965.

719 21 K. Sayama, *et al.*, *Sol. Energy Mater. Sol. Cells*, 2003, **80**, 47–71.

720 22 M. Guo, P. Diau, Y. Ren, F. Meng, H. Tian, S. Cai, *Sol. Energy Mater. Sol. Cells*, 2005, **88**, 23–35.

721 23 W. Wu, F. Meng, J. Li, X. Teng, J. Hua, *Synth. Met.*, 2009, **159**, 1028–1033.

722 24 N. Robertson, *Angew. Chem. Int. Ed.*, 2006, **45**, 2338.

723 25 CrystalClear-SM Expert, 2.0 Software Package, 2009.

724 26 A. Messerschmidt, M. Schneider, R. Huber, *J. Appl. Crystallogr.*, 1990, **23**, 436.

725 27 G. M. Sheldrick, *Acta Cryst. Sect. A*, 2007, **64**, 112.

726 28 A. L. Spek, *Acta Cryst. Sect. C Struct. Chem.*, 2015, **71**, 9.

727 29 M. J. Frisch, *et al.*, Gaussian~09 Revision D.01. Gaussian Inc. Wallingford CT, 2009.

728 30 J. F. Stanton, R. J. Bartlett, *J. Chem. Phys.*, 1993, **98**, 7029.

729 31 H.-J. Werner, *et al.*, MOLPRO, version 2012.1, a package of ab initio programs, 2012.

- 730 32 J. F. Stanton, J. Gauss, *J. Chem. Phys.* , 1994, **100**, 4695.
- 731 33 D. Kats, M. Schutz, *J. Chem. Phys.* , 2009, **131**, 124117.
- 732 34 D. Kats, T. Korona, M. Schütz., *J. Chem. Phys.* , 2006, **125**, 104106.
- 733 35 B. Hammer, L. Hansen, J. Norskov, *Phys. Rev. B* , 1999, **59**, 7413.
- 734 36 J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* , 1996, **77**, 3865.
- 735 37 J. P. Perdew, M. Ernzerhof, K. Burke, *J. Chem. Phys.* , 1996, **105**, 9982.
- 736 38 C. Adamo, C. Barone, *Chem. Phys. Lett.* , 1998, **298**, 113.
- 737 39 P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* , 1973, **28**, 213.
- 738 40 D. M. Chipman, *J. Chem. Phys.* , 2000, **112**, 5558.
- 739 41 S. Miertus, E. Scrocco, J. Tomasi, *Chem. Phys.* , 1981, **55**, 117.
- 740 42 R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* , 1980, **72**, 650.
- 741 43 M. D. Hanwell, *et al.*, *J. Cheminf.* , 2012, **4**, 17.
- 742 44 F. A. Y. N. Schröder, J. M. Cole, P. G. Waddell, S. McKechnie, *Adv. Energy Mater.* , 2015, **5**.
- 743 45 J. L. Brédas, *J. Chem. Phys.* , 1985, **82**, 3808–3811.
- 744 46 C. B. Gorman, S. R. Marder, *Proc. Natl Acad. Sci. USA* , 1993, **90**, 11 297–11 301.
- 745 47 F. H. Allen, *et al.*, *J. Chem. Soc. Perkin Trans.* , 1987, **2** p. S1.
- 746 48 F. Meyers, S. R. Marder, B. M. Pierce, J. L. Bredas, *J. Am. Chem. Soc.* , 1994, **116**, 10703.
- 747 49 T. M. Krygowski, R. Anulewicz, J. Kruszewski, *Acta Cryst. Sect. B* , 1983, **39**, 732.
- 748 50 X. Liu, Z. Xu, J. M. Cole, *J. Phys. Chem. C* , 2013, **117**, 16584.
- 749 51 J. Karolak-Wojciechowska, *Acta Cryst. Sect. B* , 1987, **43**, 574.
- 750 52 M. J. G. Peach, P. Benfield, T. Helgaker, D. J. Tozer, *J. Chem. Phys.* , 2008, **128**, 044118.
- 751 53 W. West, S. Pearce, *J. Phys. Chem.* , 1965, **69**, 1894.
- 752 54 L. Zhang, J. M. Cole, *ACS Appl. Mater. Interfaces* , 2015, **7**, 3427.
- 753 55 A. Ehret, L. Stuhl, M. T. Spitler, *The J. Phy. Chem. B* , 2001, **105**, 9960.
- 754 56 K. Higashiguchi, *et al.*, *Eur. J. Org. Chem.* , 2005, **25**, 91.
- 755 57 P. Hirva, M. Haukka, *Langmuir* , 2010, **26**, 17075.
- 756 58 T. A. Merz, P. G. Waddell, J. M. Cole, *J. Phys. Chem. C* , 2013, **117**, 8429.

- 757 59 J. McCree-Grey, J. M. Cole, P. J. Evans, *ACS Appl. Mater. Interfaces* , 2015, **7**, 16404.
- 758 60 J. M. Cole, K. S. Low, Y. Gong, *ACS Appl. Mater. Interfaces*, 2015, **7**, 27646.
- 759 61 R. S. de Armas, M. A. S. Miguel, J. Oviedo, J. F. Sanz, *Phys. Chem. Chem. Phys.* , 2012, **14**, 225.
- 760 62 R. S. de Armas, *et al.*, *J. Chem. Theory Comput.* , 2010, **6**, 2856.
- 761 63 R. S. de Armas, M. A. San-Miguel, J. Oviedo, A. Marquez, J. F. Sanz, *Phys. Chem. Chem. Phys.* , 2011,
762 **13**, 156.
- 763 64 R. S. de Armas, J. Oviedo, M. A. S. Miguel, J. F. Sanz, *J. Phys. Chem. C* , 2011, **115**, 11293.
- 764 65 L. Zhang, J. M. Cole, C. Dai, *ACS Appl. Mater. Interfaces* , 2014, **6**, 7535.
- 765 66 S. L. Bayliss, J. M. Cole, P. G. Waddell, S. McKechnie, X. Liu, *J. Phys. Chem. C* , 2014, **118**, 14082.
- 766 67 J. M. Cole, *et al.*, *Phys. Chem. Chem. Phys.* , 2014, **16**, 26684., 2015, **7**, 27646.