

Systematic Prediction of Dyes for Dye-Sensitized Solar Cells: Data Mining via Molecular Charge-Transfer Algorithms

Jacqueline M. Cole

Cavendish Laboratory, University of Cambridge

J. J. Thomson Avenue

Cambridge, CB3 0HE, UK

and

Department of Chemistry, University of New Brunswick

P.O. Box 4400

Fredericton, NB E3B 5A3, Canada

jmc61@cam.ac.uk

Graph theoretical algorithms and classification tests are combined with quantum chemical calculations and data mining tools to present successful predictions of high-performance dyes for dye-sensitized solar cells (DSCs). The construction of molecular charge-transfer algorithms is described, featuring recursive depth-first, back-tracking, graph traversal algorithms with classification test formalisms. These algorithms are employed to search through a representative set of organic chemical space (120 000 chemical molecules) to identify compounds that have the required structural attributes to act as high-performance dyes for DSCs. The first results of these predictions are validated by comparing predicted structural motifs to existing well-known dyes that are currently in use for DSC devices. Three chemical motifs are shown to form the chemical backbone of three popular dyes, thereby validating the predictions. Further work is described that includes the DSC fabrication and testing of the new classes of unknown dyes; this pertains to the ultimate goal of systematically designing new dyes for use in DSC devices.

1. Introduction to Dye-Sensitized Solar Cells

Dye-sensitized solar cells (DSCs) are one of the strongest contenders for the next generation solar cell technology. While currently less efficient than silicon-based solar cells, they are far more cost-effective to the extent that their price-performance ratio achieves grid-parity status, making them competitive with fossil fuel energy production. Furthermore, current recordings of DSC efficiencies are far from their intrinsic limit, in contrast to silicon-based solar-cell technology. The potential for improving various components of a DSC is enormous. In addition, DSCs excel in poor or ambient sunlight conditions whereas silicon-based panels are optimized for hot conditions; this makes DSC technology a particularly attractive investment for countries that have temperate weather conditions.

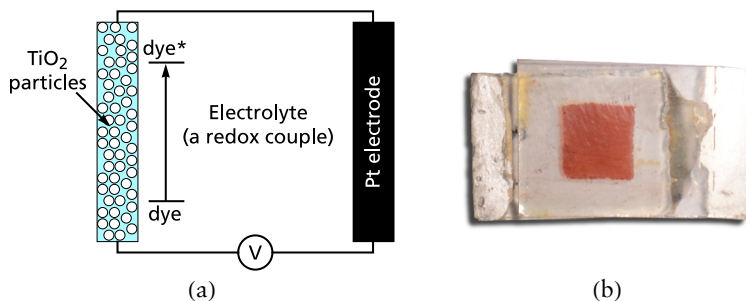


Figure 1. (a) A schematic representation of a DSC. (b) A prototype DSC device.

DSCs arose from the pioneering work of O'Regan and Grätzel and are based upon a chemical photosynthetic process [1]. In the first instance, sunlight provides the required energy ($h\nu$ photons) to promote an electron in the dye molecule from its ground-state quantum energy level to one of higher energy. So-called electronic absorption of the dye generates a photo-excited quantum state of the molecule, dye^* . The energy of this photo-excited state corresponds to that of the conducting electrons in the semiconductor, titanium dioxide (TiO_2), to which this dye is adsorbed. Such energy correspondence enables the injection of the photo-excited electron in the dye into the TiO_2 “sea of conducting electrons.” Having lost an electron, the dye molecule is said to be oxidized. Meanwhile, the TiO_2 acts as an electrode (anode) and the addition of this negative charge (e^-) into its conduction band affords a potential difference (voltage) with respect to the platinum electrode (cathode) to which it is connected. This potential difference stimulates these injected electrons to diffuse to the cathode. Sandwiched between these two electrodes is an electrolyte: a substance that yields an electron to the dye on the one hand, so regenerating the dye to its original ground-state, while gaining back an electron on the other hand from the excess electronic charge accumulating at the platinum electrode. The electrolyte is called a redox couple since this successive gain and loss of electrons is known as chemical reduction–oxidation, or redox in brief. The charge rebalancing via the electrolyte completes an electrical circuit. Figure 1(a) illustrates the circuitry while Figure 1(b) shows an example of a prototype DSC device, called a Grätzel cell after one of its inventors.

2. Materials Discovery of Dyes for Dye-Sensitized Solar Cells: A Historical Background

The efficiency of a DSC is driven by a number of factors. The molecular dye is a particularly critical component of a DSC since it is respon-

sible for both the light-harvesting of energy from the sun as well as the electron injection that initiates the chemical redox reaction of the solar cell. Consequently, there have been extensive efforts to discover new materials that outperform Grätzel's "N719" dye [1], which remains the most efficient dye for DSC operation after more than 20 years (10 to 10.4% solar cell efficiency) [2]. This is a ruthenium-based dye and, to date, only the very closely related "black dye" [3] has been able to seriously compete with N719. This said, these ruthenium-based dyes are extremely expensive relative to organic dyes. As such, economic incentives are motivating the development of efficient organic dye alternatives. Indeed, one of the most promising organic dyes has already reached 7.5% DSC efficiency [4].

One of the most important considerations of the molecular nature of the dye is its ease of transferring electronic charge across the molecule. The greater the molecular charge-transfer, the wider the range of the solar spectrum that can be absorbed by the dye. Hitherto, there has been no systematic search method for identifying dyes with sufficiently high molecular charge-transfer that affords them high performance in DSCs. Dyes that are currently used in DSC research have been discovered by chance or incremental methods (chemical substitution of *a priori* known dyes). Materials discovery is still based on serendipity or iterative chemical substitution methodologies that are based on an *a priori* known DSC active dye. Such methods are very valuable within a specific area of synthetic chemistry but they can only ever afford incremental improvements to currently known DSC dyes. Computational efforts have similarly restricted themselves to predicting or rationalizing new dyes within the framework of an existing chemical dye type [5–7]. Therefore, such methods have no capacity to reveal entirely new classes of suitable DSC dyes.

3. A Systematic Method to Predict New Classes of Dyes for Dye-Sensitized Solar Cells

If one is going to make a step-change in dye performance within DSCs, a distinct shift in the approach to dye design is therefore urgently needed that specifically targets the materials discovery of new classes of dyes. This paper aims to do precisely this, via the description of a new systematic searching method that reveals entirely new classes of dyes so as to improve DSC efficiency. This is achieved using graph theoretical analysis and classification tests, in a descriptive and predictive fashion, together with quantum-chemical calculations and data mining techniques.

3.1 Construction of Molecular Charge Transfer Algorithms

The systematic search strategy has been constructed via the development of molecular charge-transfer algorithms. In turn, these employ the concept of "molecular lego"—molecular fragments that, when

pieced together in carefully designed ways, have all the right molecular connections to afford a particular function [8]; in this case, a well-performing chemical dye.

The molecular charge-transfer algorithms require three key pieces of molecular lego: (1) the presence of suitable electron donors (D) and acceptors (A), which were classified according to a look-up table containing Hammett values, σ_r (σ is the Hammett constant, σ_r is the resonating part of σ) [9], that are derived from nuclear magnetic resonance (NMR) chemical shifts. A Hammett σ_r value is negative if the chemical substituent is electron accepting (A) and positive if it is electron donating (D). (2) π -conjugation between each D and A. For this a numerical algorithm was employed that comprises a recursive depth-first, back-tracking, graph traversal search procedure that allows all possible path traversals to be determined [10]. For each path traversal between a given D and A pair that is categorized in a fashion exemplified in Figure 2, whether or not the path is π -conjugated needs to be assessed (i.e., contains alternating single- and double-bonds or delocalized bonding that is between these two alternates).

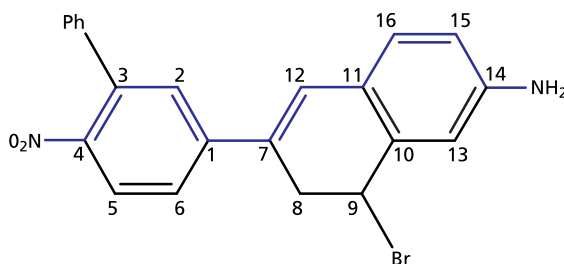


Figure 2. An example of the recursive depth-first, back-tracking graph traversal algorithm. For this chemical structure, the set of all possible conjugated NH₂NO₂ path traversals follows: {(14,15,16,11,12,7,1,2,3,4), (14,15,16,11,12,7,1,6,5,4), (14,15,16,11,10,9,8,7,1,2,3,4), (14,15,16,11,10,9,8,7,1,6,5,4), (14,13,10,11,12,7,1,2,3,4), (14,13,10,11,12,7,1,6,5,4), (14,13,10,9,8,7,1,2,3,4), (14,13,10,9,8,7,1,6,5,4)}.

Therefore, a supplementary formalism is employed in tandem with this algorithm in order to make the π -conjugation assessment. Once again, this classification strategy employs a look-up table, where the bonding types of each atom present in each molecule being searched are laid out and correlated with each path traversal numeration. If every atom involved in the traversal meets the Sybyl formalism [11] that corresponds to a conjugated atom attribute in this table, then the path traversal in question can be said to be conjugated. This search also embraces aromatic descriptors of π -conjugation, thus attending implicitly to a further DSC criterion. (3) The extent to which each π -conjugated pathway, identified in the previous search step, is delocalized. This re-

quires calculating the bond-length alternation (BLA) parameter [12], defined by

$$\text{BLA} = \sum \left(\frac{r_a}{a} \right) - \sum \left(\frac{r_b}{b} \right), \quad (1)$$

where r_a is the length of a chemical single-bond, a ; r_b is the length of the adjacent chemical double-bond, b ; and N is the total number of chemical bonds in the conjugated path, which is defined to be zero for a purely delocalized electron π -conjugated pathway.

These molecular charge-transfer algorithms were coded into the search engine of the Cambridge Structural Database (CSD) [13], which is the repository of all published organic chemical structures. In doing so, one can mine data from the entirety of this chemical space seeking molecules that possess the molecular lego in the correct configuration to afford optimal molecular charge-transfer. The search routines operate in sequential subsets according to $C \{ \pi\text{-conjugation} \} \subset B \{ \text{Donor} \cup \text{Acceptor} \} \subset A \{ \text{CSD} \}$.

3.2 Complementary Quantum-Chemical Calculations of Molecular Polarizability

In parallel with this data inquiry, quantum-chemical calculations [14] were also coupled to the search engine of the CSD such that the molecular polarization could be determined and ranked for all molecules. Such polarization represents an independent figure-of-merit for molecular charge-transfer and since high molecular charge-transfer was sought explicitly, the first nonlinear term in the polarization power series was incorporated into the calculation as well as the usual linear terms:

$$P_{\text{tot}} = \mu_i + \alpha_{ij} E_j + \beta_{ijk} E_j E_k + \gamma_{ijkl} E_j E_k E_l + \cdots \quad (2)$$

where P_{tot} = total polarization, E_j = applied electric field, μ_i = the permanent dipole moment, α_{ij} = linear polarizability, β_{ijk} , γ_{ijkl} , \cdots = first, second,... hyperpolarizability coefficients, and the subscripts i , j , and k denote tensorial components since polarizability is an anisotropic effect.

4. Validation of Results

For the purposes of this initial study, the electron acceptor was restricted to a carboxylic acid chemical group ($-\text{COOH}$) since this group is known to help the dye adsorb to the TiO_2 semiconductor component of the DSC in the device fabrication process [15]. The lists of chemicals that resulted from these independent search methods were cross correlated. The results are very encouraging since the pre-

dictions reveal structural motifs that form the chemical backbone of three dyes that are currently employed in DSC research and industry [16–19].

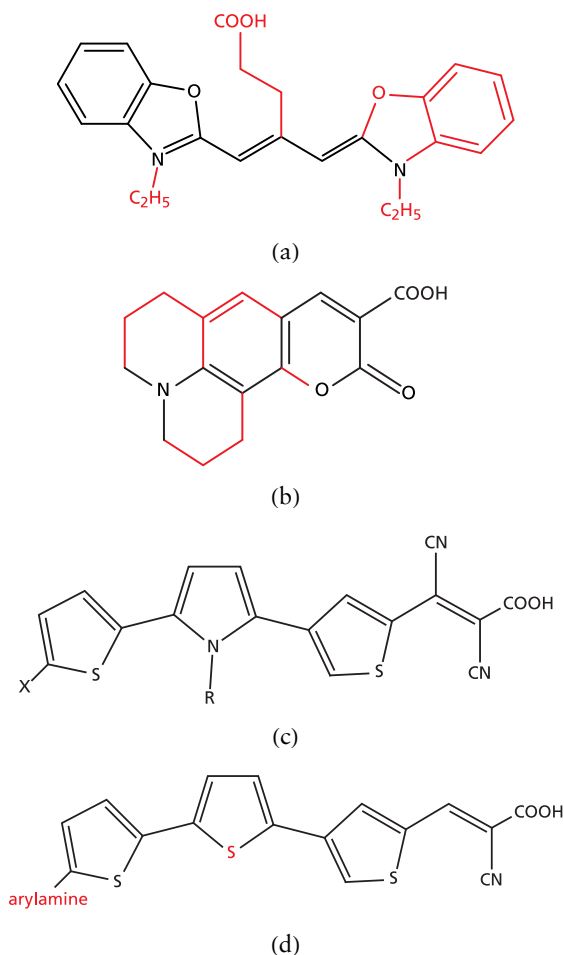


Figure 3. (a)–(c) Chemical motifs of predicted high-performance dyes (black) that form the π -conjugated chemical backbone of three commonly used dyes in current DSC research and industry. Red (gray) indicates the chemical bonds or atoms that add to these chemical motifs (black) to afford (a) an industrially marketed dye from Cyanine Technologies [16]; (b) a coumarin derivative used in research [17]; (c) a dye that bears close chemical resemblance to the dye (d) that is currently very popular amongst research groups around the world [18, 19].

The results are shown in Figure 3. The black vertices and lines represent the atoms and chemical bonds, respectively, in the predicted structural motifs. The π -conjugation is illustrated by the alternate sin-

gle- and double-bonding schematic representation of these molecules. The red (gray) vertices and lines represent the atoms and bonds that have to be added to this predicted motif in order to form a known dye. Given the dependence of π -conjugation paths in the molecular charge-transfer algorithms, these additions stand to reason. For example, all extra chemical bonds required to form molecule (a) are either (i) single and are connected by adjacent single bonds, representing a break in conjugation, or (ii) conjugated (the aromatic ring) but where such conjugation is isolated from the main conjugated chain by two successive single-bonds, that is, a break in π -conjugation. Meanwhile, all red (gray) bonds in (b) are single except for one whose importance is presumably overridden by the heteroatom (N) in the alternative (primary) conjugation path across the molecule. Compound (c) is a predicted motif that is closely matched to the commonly used dye, (d). There are no extra bonds required here to form the primary chemical molecule. Rather, the contrast here is different ring heteroatoms [S in (d) versus N-R in (c)] or different chemical substitution: an extra CN group in (c) compared with (d) and an arylamine group in (d) in place of X in (c).

5. Conclusions and Further Work

The close match of the predicted chemical motifs with these well-known dye structures provides excellent validation since good predictions should afford known, as well as unknown, high-performing dyes. Furthermore, the consistency of chemical rationalization behind observed differences corroborates the strength of these validations. The next stage is to experimentally test the unknown new classes of dyes that are revealed by these predictions.

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References

- [1] B. O'Regan and M. Grätzel, "A Low-Cost, High-Efficiency Solar Cell Based on Dye-Sensitized Colloidal TiO₂ Films," *Nature*, 353, 1991 pp. 737–740. doi:10.1038/353737a0.

- [2] M. A. Green, K. Emery, Y. Hishikawa, and W. Warta, "Solar Cell Efficiency Tables (Version 37)," *Progress in Photovoltaics*, 19(1), 2011 p. 84. doi:10.1002/pip.1088.
- [3] M. K. Nazeeruddin, P. Pechy, and M. Grätzel, "Efficient Panchromatic Sensitization of Nanocrystalline TiO_2 Films by a Black Dye Based on a Trithiocyanato-Ruthenium Complex," *Chemical Communications*, 18, 1997 pp. 1705–1706. doi:10.1039/a703277c.
- [4] T. Daeneke, T.-H. Kwon, A. B. Holmes, N. W. Duffy, U. Bach, and L. Spiccia, "High-Efficiency Dye-Sensitized Solar Cells with Ferrocene-Based Electrolytes," *Nature Chemistry*, 3, 2011 pp. 211–215. doi:10.1038/nchem.966.
- [5] F. De Angelis, S. Fantacci, A. Selloni, M. K. Nazeeruddin, and M. Grätzel, "First-Principles Modeling of the Adsorption Geometry and Electronic Structure of Ru(II) Dyes on Extended TiO_2 Substrates for Dye-Sensitized Solar Cell Applications," *Journal of Physical Chemistry C*, 114(13), 2010 pp. 6054–6061. doi:10.1021/jp911663k.
- [6] S. Meng, E. Kaxiras, M. K. Nazeeruddin, and M. Grätzel, "Design of Dye Acceptors for Photovoltaics from First-Principles Calculations," *Journal of Physical Chemistry C*, 115(18), 2011 pp. 9276–9282. doi:10.1021/jp201646q.
- [7] M. Pastore, E. Mosconi, F. De Angelis, and M. Grätzel, "A Computational Investigation of Organic Dyes for Dye-Sensitized Solar Cells: Benchmark, Strategies, and Open Issues," *Journal of Physical Chemistry C*, 114(15), 2010 pp. 7205–7212. doi:10.1021/jp100713r.
- [8] J. M. Cole, "Organic Materials for Second-Harmonic Generation: Advances in Relating Structure to Function," *Philosophical Transactions of the Royal Society A*, 361, 2003 pp. 2751–2770. doi:10.1098/rsta.2003.1271.
- [9] L. P. Hammett, "The Effect of Structure Upon the Reactions of Organic Compounds. Benzene Derivatives," *Journal of the American Chemical Society*, 59(1), 1937 pp. 96–103. doi:10.1021/ja01280a022.
- [10] R. Sedgewick, *Algorithms in C++: Part 5, Graph Algorithms*, 3rd ed., Boston: Addison-Wesley, 2002.
- [11] M. Clark, R. D. Cramer III, and N. van Opdenbosch, "Validation of the General Purpose Tripos 5.2 Force Field," *Journal of Computational Chemistry*, 10(8), 1989 pp. 982–1012. doi:10.1002/jcc.540100804.
- [12] S. R. Marder and J. W. Perry, "Molecular Materials for Second-Order Nonlinear Optical Applications," *Advanced Materials*, 5(11), 1993 pp. 804–815. doi:10.1002/adma.19930051104.
- [13] F. H. Allen, "The Cambridge Structural Database: A Quarter of a Million Crystal Structures and Rising," *Acta Crystallographica B*, 58, 2002 pp. 380–388. doi:10.1107/S0108768102003890.
- [14] MOPAC 2002, J. J. P. Stewart, Fujitsu Limited, Tokyo, Japan, 1999.
- [15] K. S. Low, J. M. Cole, X. Zhou, and N. Yufa, "Rationalizing the Molecular Origins of Ru and Fe-Based Dyes for Dye-Sensitized Solar Cells," *Acta Crystallographica B*, forthcoming.
- [16] Cyanine Technologies, The 2011 Catalogue of Organic Dyes for Solar Cells (May 16, 2011).

- [17] K. Hara, T. Sato, R. Katoh, A. Furube, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, and H. Arakawa, "Molecular Design of Coumarin Dyes for Efficient Dye-Sensitized Solar Cells," *Journal of Physical Chemistry B*, **107**(2), 2003 pp. 597–606. doi:10.1021/jp026963x.
- [18] K. R. J. Thomas, Y.-C. Hsu, J. T. Lin, K.-M. Lee, K.-C. Ho, C.-H. Lai, Y.-M. Cheng, and P.-T. Chou, "2,3-Disubstituted Thiophene-Based Organic Dyes for Solar Cells," *Chemistry of Materials*, **20**(5), 2008 pp. 1830–1840. doi:10.1021/cm702631r.
- [19] R. Katoh, A. Furube, S. Mori, M. Miyashita, K. Sunahara, N. Koumura, and K. Hara, "Highly Stable Sensitizer Dyes for Dye-Sensitized Solar Cells: Role of the Oligothiophene Moiety," *Energy and Environmental Science*, **2**, 2009 pp. 542–546. doi:10.1039/B900372J.