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The fuzziness of a chromogenic spirooxazine

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ABSTRACT

Science is urged to win the Complexity Challenges. One strategy to reach this goal consists in developing Artificial Intelligence because the human nervous system is a prototype of Natural Complex System that can solve few Computational Complexity problems quite easily. To try to understand human intelligence at the "implementation level", we are proposing chromogenic compounds as surrogates of natural sensory elements. Since Fuzzy logic is the best model of human ability to compute with words, two methodologies to implement Fuzzy logic by a chromogenic spirooxazine are described. Moreover, a new definition of Colourability of a chromogenic material, based on the mathematical Theory of Information, is presented.

1. Introduction

Nowadays, science is trying to win the Complexity Challenges. There are two different types of Complexity Challenges. The first type regards everyday life and consists in a deep understanding and a reliable prediction of the behaviour of Natural Complex systems. Examples of Natural Complex systems are the living beings (both unicellular and pluricellular), ecosystems, the climate, human brain, any social and economic organization, and so on. The second type of challenges concerns about the Computational Complexity, i.e. the accurate solutions of NP-problems and the recognition of variable patterns, like human faces, voices, hand-written cursive words, etc… To try to win at least few Complexity Challenges, scientists are exploiting three different strategies.

The first strategy consists in developing always more powerful supercomputers [1], because facing Complexity means in general handling a huge number of data. In June 2013, the TOP500 Project announced that the fastest supercomputer in the world is the Chinese Tianhe-2, reaching an astonishing computational rate of 33.86 petaflop/s, and with a memory of one million of GB. According to TOP500 Project, a computational rate of one exaflop/s would be within reach in 2018. This will make easier to address issues regarding Natural Complex Systems.

The second strategy is the interdisciplinary research known as Natural Computing [2]. It involves computer scientists, biologists, chemists, physicists, engineers, and its aim is to propose new algorithms and new materials to cope with the Computational Complexity Challenges, and new models to describe the systems of Natural Complexity.

Finally, there exists a third strategy which consists in developing Artificial Intelligence. The researchers working in the field of Artificial Intelligence are driven by the ambitious project of understanding the foundations and running mechanisms of human mind in order to try to reproduce them artificially. Any relevant success in the field of Artificial Intelligence would have positive impact on the challenges to Complexity. In fact, it would unveil at least a few secrets of Natural Complexity, because the human brain is a prototype of Complex Systems. Moreover, it would give new tools to face the challenges of Computational Complexity such as those encompassed under the name of pattern recognition because human mind is good at recalling variable patterns.

In a fairly recent book [3], the cognitive scientists Gallistel and King, in agreement with the neuroscientist Marr [4], argue that to understand a complex biological system like our brain, it is necessary to perform an analysis at three distinct levels. The first is the "computational level" and consists in describing the inputs, outputs and the task of the system. The second is the "algorithmic level" and consists in formulating algorithms that might carry out those computations. Finally, the third is the "implementation level" and consists in searching for mechanisms of the kind that would make the algorithm work. In our group, we are following the methodology proposed by Gallistel, King and Marr, to develop

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Chemical Artificial Intelligence [5]. We are analyzing the Human Nervous System at the three levels. At the "computational" and "algorithmic" levels, we are proposing an integration of Fuzzy logic with Bayesian probabilistic theory as a model of human inference [5,6]. At the "implementation" level, chromogenic compounds and the Belousov Zhabotinsky reaction [7,8] are proposed as surrogates of sensory and neural cells, respectively. We believe that the Chemical Artificial Intelligence will approach the human abilities of (i) taking decisions in Complex situations and (ii) recognizing variable patterns, if it processes Fuzzy logic. In fact, Fuzzy logic is a good model of the human power of "computing" with words.

In this paper, a definition of Colourability of chromogenic materials, based on the Shannon's theory [9], is proposed as quantification of the amount of information the chromogenic compounds send to an human eye. Then, the fundamentals of Fuzzy logic are outlined, and two different methodologies for implementing Fuzzy logic with the chromogenic 1,3-dihydro-1,3,3-trimethyl-8′-nitrospiro[2H-indole-2,3′-[3H]naphth[2,1-b][1,4]oxazine] (SpO) are described. The first methodology consists in handling the conformational substates of the compound and their dependence on external physical and chemical conditions. The second methodology consists in exploiting non-linear, smooth, macroscopic input–output relations to implement the fundamental fuzzy logic operators, AND, OR, NOT in analogy to what happens in micro-electronics [10–13].

The strategies proposed here for processing Fuzzy logic by using a chromogenic compound will be extended to other types of compounds and chemical reactions in the next future.

2. Materials and methods

The description of the Materials and the Experimental Methods used to collect the data that have been processed in this work may be found in Refs. [13,14]. Below, I describe the Computational Methods.

To transform the transmittance spectra in chromaticity coordinates x, y, z the following procedure has been used [15]. First of all, the CIE XYZ tristimulus values have been calculated through the integrals

$$\begin{aligned} X &= \frac{1}{k}\int_{360}^{800} D(\lambda)T(\lambda)\bar{x}(\lambda)\mathrm{d}\lambda \\ Y &= \frac{1}{k}\int_{360}^{800} D(\lambda)T(\lambda)\bar{y}(\lambda)\mathrm{d}\lambda \\ Z &= \frac{1}{k}\int_{360}^{800} D(\lambda)T(\lambda)\bar{z}(\lambda)\mathrm{d}\lambda \end{aligned} \tag{1}$$

wherein $\bar{x}, \bar{y}, \bar{z}$ are the colour-matching functions whereby the CIE (Commision Internationale de l'Éclairage) standardized the sensitivity of human eye in 1964; $D(\lambda)$ is the energy distribution of the CIE normalized illuminant D65 (which closely matches that of the sky daylight); $T(\lambda)$ is the transmittance spectrum, and k is a normalization factor defined in such a way that a sample with a uniform transmittance $T(\lambda) = 1$ for $\lambda \in [360-800]$ gives a luminance component $Y = 1$:

$$k = \int_{360}^{800} D(\lambda)\bar{y}(\lambda)\mathrm{d}\lambda \tag{2}$$

Then the chromaticity coordinates are calculated as follows:

$$\begin{aligned} x &= X/(X+Y+Z) \\ y &= Y/(X+Y+Z) \\ z &= Z/(X+Y+Z) \end{aligned} \tag{3}$$

From equation (3), it derives that $x + y + z = 1$.

The XYZ tristimulus values have been transformed into the RGB coordinates by the following linear transformation

$$\begin{bmatrix} R \\ G \\ B \end{bmatrix} = \begin{bmatrix} 3.240479 & -1.537150 & -0.498535 \\ -0.969256 & 1.875992 & 0.041556 \\ 0.055648 & -0.204043 & 1.057311 \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} \tag{4}$$

The RGB values should stay between 0 and 1. In some cases they were slightly greater than 1. In these cases, the values were rounded to 1. The final step was to scale the RGB values obtained from (4) to values included between 0 and 255 [15].

The XYZ tristimulus values have been transformed into the CIE $L^*a^*b^*$ coordinates by the following algorithms based on the values of tristimulus determined for the reference white ($X_W = 0.94811$, $Y_W = 1$, $Z_W = 1.0730$):

$$L^* = 116\left(\frac{Y}{Y_W}\right)^{1/3} - 16 \qquad \text{for } (Y/Y_W) > 0.008856 \tag{5}$$

$$L^* = 903.3(Y/Y_W) \qquad \text{otherwise} \tag{6}$$

$$\begin{aligned} a^* &= 500\left(f\left(\frac{X}{X_W}\right) - f\left(\frac{Y}{Y_W}\right)\right) \\ b^* &= 200\left(f\left(\frac{Y}{Y_W}\right) - f\left(\frac{Z}{Z_W}\right)\right) \end{aligned} \tag{7}$$

where $f(t) = t^{1/3}$ for $t > 0.008856$, whereas $f(t) = 7.787t + 16/116$ otherwise.

The CIE $L^*a^*b^*$ coordinates can be transformed in CIE $L^*C^*h^*$ coordinates by these simple algorithms:

$$\begin{aligned} L^* &= L^* \\ C^* &= \sqrt{a^{*2} + b^{*2}} \\ h^* &= \arccos\left(\frac{a^*}{C^*}\right) = \arcsin\left(\frac{b^*}{C^*}\right) \end{aligned} \tag{8}$$

The thermal bleaching kinetics ($A(t)$) characterizing the photochromic behaviour of 1,3-dihydro-1,3,3-trimethyl-8′-nitro-spiro [2H-indole-2,3′-[3H]naphth[2,1-b][1,4]oxazine] (SpO) have been analysed by the Maximum Entropy Method (MEM) using the MemExp Software available online [16,17]. In the Maximum Entropy Method, an experimental kinetics $A(t)$ is fitted by the following function:

$$A(t) = D_0 \int_{-\infty}^{+\infty} \mathrm{d}\log\tau[g(\log\tau) - h(\log\tau)]\mathrm{d}t' e^{-(t_i - t^*)/\tau} + \sum_{k=0}^{3}(b_k - c_k) \tag{9}$$

where $g(\log\tau)$ and $h(\log\tau)$ are the lifetime distributions that correspond to decay and rise kinetics, respectively, and the polynomial term accounts for the baseline. The fit procedure entails the maximization of the function Q defined in equation (10):

$$Q = S - \lambda C - \alpha I \tag{10}$$

wherein S is entropy defined as $S(\vec{f}, \vec{F}) = \sum_{j=1}^{M}[f_j - F_j - f_j \ln(f_j/F_j)]$ where f is the image that includes both the g and the h lifetime distributions, whereas F is the MEM prior distribution used to