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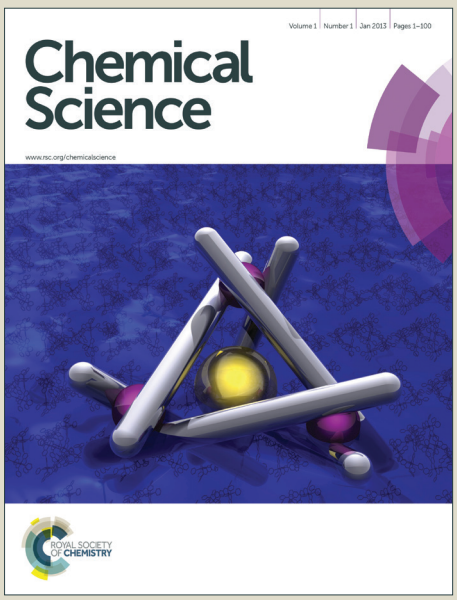





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ARTICLE

# A Continuous and Multi Valued System as Molecular Answer for Data Processing and Data Storage

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A molecular logic system with a quaternary basis as well as a continuous system as an alternative related to logic concepts was made accessible. Both systems are based on a mixture of benzonitrile oxide, iron(III) chloride and either zinc or sodium thiocyanate, analysable by photography and subsequent RGB value analysis with a common image processing software. The quaternary logic system increases the possible amount of data processing by raising the arithmetic basis whereas the continuous system could extend the world of multi valued logic to real floating point operations with unprecedented precision. Additionally both systems are long-term stable and could for example be used as high potential storage medium with a high data processing.

## Introduction

Nowadays the demand for processing of information required in nearly every application rises with simultaneous decrease in the desired size.[1] Even with an improved design miniaturization raises problems, for instance excessive heat formation when the electric conductance or power is retained.[2,3] Classical systems of information processing based on silicon circuits using binary (boolean) logic are susceptible to Moore's law which predicts that the number of transistors in silicon microprocessors double every 18 months.[4] Even with application of new materials the performance of electronic devices is limited as a result of technological barriers.[2] Arithmetic systems based on molecules on the other hand offer a greater degree of versatility due to the synthetic accessible range of molecular structures[5] and the achievable information density per mole material is only limited by Avogadro's number. Traditional silicon logic systems use a binary number system which encodes all information in series of zeros and ones, expressed as low and high potential values.[2] On a molecular level there is no reason to be restricted to binary systems which indicates the presence or absence of a substance. Based on the chemical behaviour few examples of ternary molecular systems addressed by their spectroscopic (mostly fluorescence) response upon interaction with electronically inputs[6,7], chemical inputs[8], change in the pH value[9,10] or in the metal ion to ligand ratio[11] as well as by their electronic behaviour (e.g. semiconductor[12,13], quantum dots[14]) are well known besides a wide range of binary molecular systems. [9,15-30] In a ternary system, three different states for output signals can be defined, for instance 0 for a low, 1 for a medium and 2 for a high signal or -1, 0 and +1, respectively.[8] An increase from a binary to a ternary logic system is an advantage because a binary system needs in theory 1.59-times more components per gate for the same calculation as a ternary system.[31] Thus a ternary or even higher valued system could be an opportunity for a higher information processing density at constant size.[8,31] But the gain obtained by the molecular approach could be even more than by a multi valued system. This could be the realization of an alternative concept related to logics.[8,32] Molecular interaction allows establishing a more flexible and continuous system. Thus it is worthwhile to reconsider if information processing has to be restricted to defined states like 0's and 1's. Or could it be even proceeded to a continuous system where the output is represented by a continuous value or floating point number.[33] This would facilitate an extraordinary boost in information processing and maybe enhance the way of computerization beyond the state of the art. Here we present a molecular system which enfolds a quaternary calculation base and on the other hand a continuous system which can be coupled to a ternary logic system to achieve an additional calculation enhancement. Both systems are based only on their reagents and chemical behaviour with a clear and defined design, which makes them highly attractive. Certainly, they require further developments to achieve the various logic architectures already realised by other groups, e.g. van der Boom[1,6,7,28] or de Silva[9,29,34,35]. But even in its current stage they could already by used as chemical system for data storage and although multi valued systems are prone to error accumulation during serial operations,[1,36] what so far restricted their application in conventional computing and data processing, it is a possible application and especially in combination with the continuous system it could promise to open new avenues in the design of molecular logic systems.

## Results and discussion

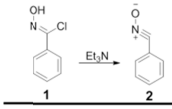
We designed a system with two inputs, which provide up to four different states, which can be characterized by RGB value analysis[37-39] using an image processing software. Therefore we identified benzonitrile oxide, iron(III)-ions and either zinc for the quaternary or thiocyanate-ions for the continuous system as suitable components.

As dye system benzonitrile oxide (**2**) is generated in situ by treating of hydroxybenzimidoyl chloride (**1**) with triethylamine. In the applied concentration range triethylamine had no influence on the colour proofed by reference measurements without hydroxybenzimidoyl chloride (**1**), but was required to achieve complete conversion to benzonitrile oxide (**2**).

**Quaternary Logic System**

In a first step we realised a molecular system with up to four different states based on a complexation of benzonitrile oxide with iron(III)-ions, which gives a deeply purple coloured dye.[40] In presence of zinc the iron(III) is reduced to iron(II) which shows a less intense colour in combination with benzonitrile oxide. Additionally zinc(II), formed in this redox reaction leads to insoluble iron complexes independent of the oxidation state of the iron cations. Putting all these components together we get a constitutional-map depicted in Table 1 with the assigned colour values tabulated in Table 2. This Tables show that four different states are analysable. State A represents a colourless state with the R values between 170 and 220, G between 170 and 250 and B between 150 and 200, which indicates the absence of iron(III) or occurs only with iron(III) in combination with neither benzonitrile oxide nor zinc. State B is yellow and indicates the presence of 24 mmol zinc, 30 mM iron(III) and no benzonitrile oxide (R: 200-250, G: 150-200, B: 50-100). The last single-coloured state is C, which is deep purple and occurs with 20 mM benzonitrile oxide, 30 mM iron(III) and no zinc (R/G/B: 0-50). The combination of 30 mM iron(III) and 20 mM benzonitrile oxide with at least 24 mmol zinc or with more than 60 mmol zinc without benzonitrile oxide results in a precipitate. This could be easily determined by taking two averaged RGB values for each solution, one at top and one at the bottom of the cuvette. For every RGB value taken an average of at least 50 square pixels was used. To make this machine readable we defined the following limits for the deviation of the RGB values: For state A to C the deviation between the R, G or B value of the top or the bottom of the solution is under 30, for state D it is over 30, clearly indicating a precipitate.

**Table 1** Table of the assignment in the benzonitrile oxide/iron/zinc-system.




| | Fe(III) | Zn | | |
|---|---|---|---|---|
| | | 0 | 24mmol | 60mmol |
| 0 | 0 | State **A** | | |
| 20mM | 0 | | | |
| 0 | 30mM | | State **B** | |
| 20mM | 30mM | State **C** | | State **D** |

**Table 2** Table of possible colour values in the benzonitrile oxide/iron/zinc-system.

| | | State | | | |
|---|---|---|---|---|---|
| | | A | B | C | D |
| RGB value | R | 170-220 | 200-250 | 0-50 | Deviation of R, G or B between >30 top and bottom phase |
| | G | 150-250 | 150-200 | 0-50 | |
| | B | 150-200 | 50-100 | 0-50 | |
| Picture of an example cuvette | |  |  |  |  |

With this map in hands it is now possible to build discrete valued systems with up to two input components while the third component remains constant (**F**igure 1). As possible binary logic system the truth tables I to III (Figure 1) could be determined, which represent in all cases classical AND gates. For I no zinc is present so the ground state is A, which could represent a 0 in a binary system. Only if iron(III) with a concentration of 30 mM in addition to benzonitrile oxide (20 mM) is present state C as a 1 in a binary system is detectable. Following the same principle for II benzonitrile oxide has to be absence and only if 30 mM iron(III) and 24 mmol zinc is present state B occurs, representing a 1 in a binary system. For III the amount of zinc is increased to 60 mmol at a constant benzonitrile oxide concentration of 20 mM switching to state D instead from state B. For the ternary valued systems the truth tables IV and V are applicable as depicted in Figure 1. In both cases the states A, C and D are selectable. For truth table IV benzonitrile oxide has to be present in a 20 mM concentration and zinc and iron(III) are variable between 0 and 24 mmol for zinc and 0 and 30 mM for iron(III), respectively. Without iron(III) only state A is present, with iron(III) this state can switch to state C without zinc and D with zinc. In truth table V the iron(III) concentration is fixed at 30 mM whereas benzonitrile oxide is varied between 0 and 20 mM and zinc between 0 and 60 mmol. Only in presence of zinc state D occurs. If there is no zinc available state A in absence and state C in presence of benzonitrile oxide is detectable. The highest value achievable with this setup is four, shown in truth table VI. Here, the iron(III) concentration is constant at a level of 30 mM and by a benzonitrile oxide concentration varying between 0 and 20 mM and the amount of zinc between 0 and 24 mmol it is possible to select and differentiate the four states A, B, C and D. Thereby the presented setup allows creating a quaternary logic system, which intrinsically offers a high information processing density. Additionally it is flexible enough to switch between multi valued systems, for instance between truth table V and VI by only raising the modulated zinc concentration in order to switch between a ternary and a quaternary valued system. Apart from that all elements contain aqueous solutions this system is long-term storable without colour loss. It is interesting to note that in a dried status, which further increases the information density by decreasing the overall volume, the long-term stability further increases and it is possible to read out the data after adding a defined amount of water.

$2^n$

| I | Fe(III) [mM] 0 | 30 |
|---|---|---|
| Nitr. [mM] 0 | A | A |
| 20 | A | C |

| II | Fe(III) [mM] 0 | 30 |
|---|---|---|
| Zn(0) [mmol] 0 | A | A |
| 24 | A | B |

| III | Fe(III) [mM] 0 | 30 |
|---|---|---|
| Zn(0) [mmol] 0 | A | A |
| 60 | A | D |

$3^n$

| IV | Zn [mmol] 0 | 24 |
|---|---|---|
| Fe(III) [mM] 0 | A | A |
| 30 | C | D |

| V | Zn [mmol] 0 | 60 |
|---|---|---|
| Nitr. [mM] 0 | A | D |
| 20 | C | D |

$4^n$

| VI | Zn [mmol] 0 | 24 |
|---|---|---|
| Nitr. [mM] 0 | A | B |
| 20 | C | D |

**Fig. 1** Possible truth tables for binary (I-III), ternary (IV-V) and quaternary (VI) valued logic systems based on the presented setup depicted in Table 1. Nitr. = benzonitrile oxide. For I zinc is constant at 0 mol, for II benzonitrile oxide is 0 mM, for III and IV benzonitrile oxide is 20 mM, for V and VI iron(III) is 30 mM.

**Continuous System**

Next to the quaternary valued system we developed the idea of a continuous logic system to create the basis for an alternative information system able to process floating point operations. When benzonitrile oxide (**2**) is mixed with sodium thiocyanate a deeply red complex is formed, which is soluble in diethyl ether.[40] We used this property to design a more flexible system consisting of benzonitrile oxide (constant at a concentration of 10 mM), iron(III) and thiocyanate ions in a two phase composition (water and diethyl ether). In the aqueous phase three states can be realised $A_{SCN}$, $B_{SCN}$ and $C_{SCN}$ (Figure 2; for a better differentiation of the quaternary valued zinc containing system these states were denoted by the subscript "SCN"). The empirically set borders for the states in the aqueous phase are relatively similar to the states of the quaternary system (*vide supra*) with the only difference that no precipitation occurs, thus state $D_{SCN}$ can be neglected.

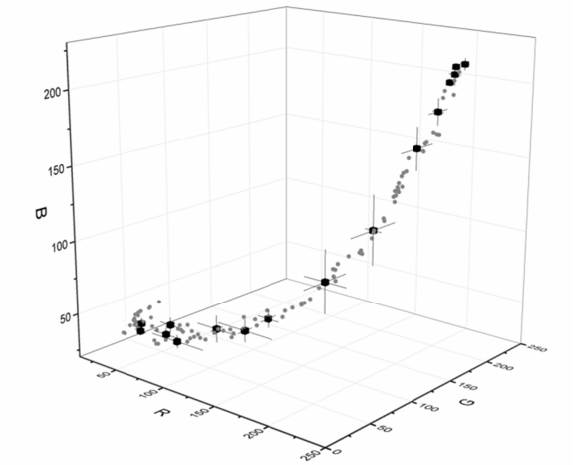



**Fig. 3** RGB space of the organic phase at 10 mM iron(III) and 0 to 40 mM thiocyanate. As grey dots a dilution series of the iron-thiocyanate-complex is depicted and in black the measured benzonitrile oxide/iron/thiocyanate samples (averaged values with error bars).

In the organic phase three states can be realised: Two steady like states $A'_{SCN}$ and $C'_{SCN}$ (the subscript "'" denotes the organic phase) which are very similar to the aqueous phase from an analytical point of view and a continuous state $B'_{SCN}$. In Figure 3 the RGB values for the organic phase at a concentration of 10 mM iron(III) and 0 to 40 mM thiocyanate are depicted. It is possible to determine the dependence on each RGB value to the thiocyanate concentration (exemplary depicted for the R value in Figure 4). For each RGB value it starts with a constant state $A'_{SCN}$ followed by a linear dependence (state $B'_{SCN}$) and ends with a constant state $C'_{SCN}$.

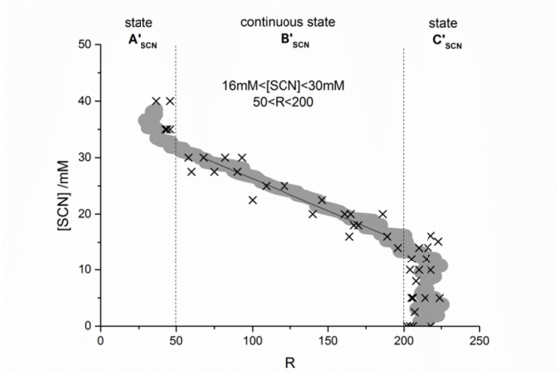



**Fig. 4** The evaluated R values in dependence on the thiocyanate concentration. In grey a dilution series of the iron-thiocyanate-complex is depicted as probability distribution band and in black the measured benzonitrile oxide/iron/thiocyanate samples are shown.

There are different borders of the linear part for the R, G and B values caused by the different sizes of the steady like states $A'_{SCN}$ and $C'_{SCN}$ for each of them (Table 3). Based on this calculations it is possible to determine the thiocyanate concentration from the measured RGB values within a concentration range between 10 and 30 mM thiocyanate. Hereby, the concentration range of thiocyanate from 10 to 18 mM is provided by the G value, in addition from 10 to 20 mM by the B value and finally the R value extends the range up to 30 mM (data is tabulated in Table 3 and also graphically depicted on the right side of Figure 2). Several repetitions of these measurements demonstrated that the calculations are within a maximum deviation of ±3mM (based on more than 50 independent measurements). In Figure 3 and 4 a dilution series of an iron(III)-thiocyanate-complex in diethyl ether is depicted (in grey) next to the measured samples. The measured RGB values are all located within this dilution series. This in turn results in a small empirical error. Van der Boom *et al.* published in 2010 a multiple state system based on the polymer poly(3,4-ethylenedioxythiophene) (PEDOT) deposited on indium thin oxide (ITO) coated glass.[6] They used optical absorbance as output signal (λ=630 nm), or more precisely its deviation from the undoped state and identified by increasing the potential from -0.6 to 0.6 V a sigmoidal dependence between the absorbance deviation and the applied potential. Based on particular chosen potential values they can create up to five stable logic states (binary, ternary, quaternary and quinary). Nevertheless, due to the sigmoidal dependence they have to address defined systems (multiple system) in between they can shift, but a fully continuous system like we present would be highly error-prone and impair the accuracy of the

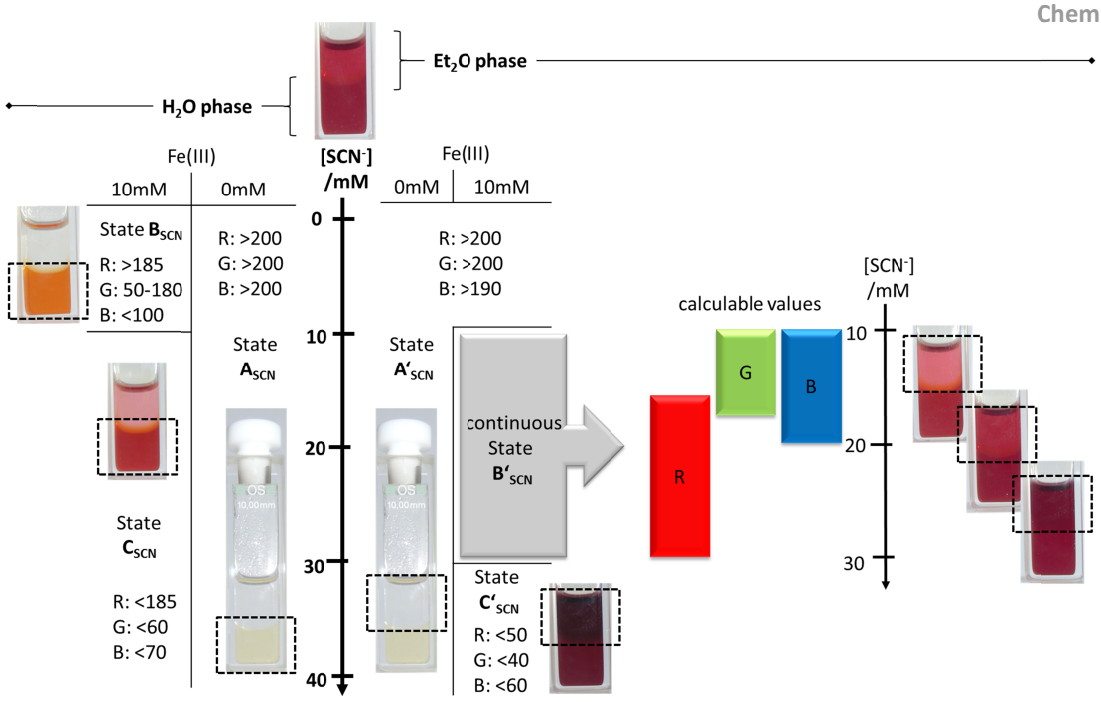



**Fig. 2** Map of the possible values of the benzonitrile oxide/iron/thiocyanate-system. The benzonitrile oxide concentration is kept constant at a level of 10 mM.

input-output-correlation. Caused by the linear dependence of our system a continuous treatment is feasible also considering the determined empirical errors (Table 3).

**Table 3** Equations and statistical analysis for the linear part of the state $B'_{SCN}$, the fitted values and borders of the linear states $B'_{SCN}$ to $A'_{SCN}$ and $C'_{SCN}$. y: thiocyanate concentration, x: R, G or B value.

| | $y = a + b * x$ | | Borders | |
|---|---|---|---|---|
| | a | b | $[SCN^-]$ /mM | R/G/B value |
| **R** | 330.70±19.64 | -8.78±0.83 | 16-30 | 50-200 |
| **G** | 363.55±35.43 | -17.81±2.51 | 10-18 | 40-200 |
| **B** | 314.48±24.36 | -13.06±1.58 | 10-20 | 60-190 |

The aqueous and the diethyl ether phase are associated with each other as depicted on the left side of Figure 2. Thus the states A' and $A'_{SCN}$ are coexistent. In presence of iron(III) $A'_{SCN}$ is associated with $B_{SCN}$ and $C_{SCN}$ is connected with the continuous state $B'_{SCN}$ and $C'_{SCN}$. Hence a coupled interpretation of the aqueous and organic phase leads to no information enhancement but establishes the opportunity to have two systems - a classical ternary valued logic system and a continuous system - in a single setup which can be used alternatively or simultaneously. Both systems are only apart by a slight shift of the observation window from one phase to the other. The ternary system with thiocyanate could, as described for the quaternary system with zinc, increase the amount of processable data by raising the arithmetic basis. The continuous part could extend the classical binary logic or even multi valued logic to a continuous concept related to logics. Within a continuous system several different states could be triggered thereby it would increase the information processing density rapidly. Additionally the presented continuous system is coupled with a "steady" ternary valued logic system allowing an easy switch between two different systems or a simultaneous use. Additionally all described chemical systems are very long-term stable and with the known dilution factor also storable for many years. Such storage would be unsusceptible to magnetic fields or other forces. As pointed out, the dried mixture could be unlimitedly dissolved, decoded and restored at any time. So the presented systems could be used as a high potential nearly indestructible storage medium with a high data processing density.

## Experimental

Hydroxybenzimidoyl chloride (**1**) was synthesized according to Hall *et al.*.[41] For the measurements hydroxybenzimidoyl chloride (**1**), iron(III) chloride, zinc and/or sodium thiocyanate were solved in water with or without diethyl ether (according to the desired conditions in Table 1 and Figure 2) and treated with triethylamine for *in situ* generation of benzonitrile oxide (**2**). The amount of zinc was 0, 24 and 60 µmol per mL water. The reaction flask was sealed and stirred at room temperature for two hours. The reaction mixture was transferred into quartz cuvettes and photos were light-protected be shot by a Casio EX-ZR300 camera at a distance of 10 cm. Focal aperture (F/3), obligatory flash and film sensitivity (ISO 80) were kept constant. The photos were analysed by GIMP2 (a commercial image processing software) by measuring the RGB values of the average of nearly 50 square pixels. For the benzonitrile oxide/iron/zinc-system the RGB values of the top and bottom of the aqueous phase were determined and for the benzonitrile oxide/iron/thiocyanate-system the centre of the aqueous and of the organic phase were used.

## Conclusions

Based on a mixture of benzonitrile oxid, iron(III) chloride and either zinc or sodium thiocyanate we presented a ternary/ quaternary valued logic system as well as a continuous system for data processing, both working with two input factors. Both



systems are simply analysable by photography and a common image processing software to determine the corresponding RGB values which could be directly used as arithmetic value. The quaternary valued logic system increases the possible amount of data processed by raising the arithmetic basis whereas the continuous system could extend the world of multi valued logic to a continuous concept related to logics. In the continuous system several different states could be triggered and thereby it increases the information processing density rapidly. Beside their potential improvement in the area of data processing both systems are long-term stable and could already be used as a high potential storage medium (e.g. as write-once read-many-times (WORM) memory devices) with a high data processing density which is unsusceptible to magnetic fields or mechanic forces.

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## Notes and references

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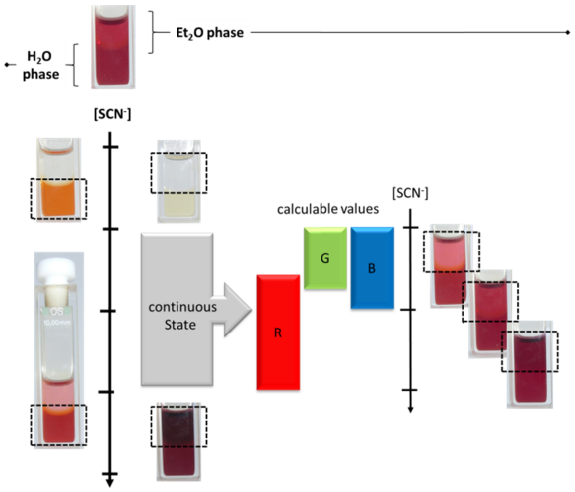
## TOC Figure




Two molecular logic systems are presented with two independent input factors resulting in a continuous system and a system with a quaternary basis.