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Molecular level all-optical logic with chlorophyll absorption spectrum and polarization sensitivity

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ABSTRACT Chlorophyll is suggested as a suitable medium for realizing optical Boolean logic at the molecular level in view of its wavelength-selective property and polarization sensitivity in the visible region. Spectrophotometric studies are made with solutions of total chlorophyll and chromatographically isolated components, viz. chlorophyll a and b and carotenoids extracted from pumpkin leaves of different maturity stages. The absorption features of matured chlorophyll with two characteristic absorption peaks and one transmission band are molecular properties and independent of concentration. A qualitative explanation of such an absorption property is presented in terms of a 'particle in a box' model and the property is employed to simulate two-input optical logic operations. If both of the inputs are either red or blue, absorption is high. If either one is absent and replaced by a wavelength of the transmission band, e.g. green, absorption is low. Assigning these values as 0 s or 1 s, AND and OR operations can be performed. A NOT operation can be simulated with the transmittance instead of the absorbance. Also, the shift in absorbance values for two different polarizations of the same monochromatic light can simulate two logical states with a single wavelength. Cyclic change in absorbance is noted over a rotation of 360° for both red and blue peaks, although the difference is not very large. Red monochromatic light with polarizations apart by 90°, corresponding to maximum and minimum absorption, respectively, may be assigned as the two logical states. The fluorescence emissions for different pigment components are measured at different excitation wavelengths and the effect of fluorescence on the red absorbance is concluded to be negligible.

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1 Introduction

Realization of electronic devices at molecular level has been a subject of interest for the last few decades, as reviewed in the literature [1–4]. In addition to innovation in conventional top-down approaches and investigation with semiconductor devices [5], researches were carried out on bottom-up approaches with molecular and supramolecular structures of different materials [4, 6–21]. One of the most widespread investigations was done on realization of Boolean logical operations coded in terms of chemical signals [4, 8], optical signals [6, 7, 9–13] and quantum logic with single photons [14] and wave properties of electrons [15, 16]. The above are implemented with wide varieties of materials and device mechanisms including simple [9] and complex [10] logic implementation with pump–probe stimulation of isolated molecules, pulsed irradiation of thin films of organic molecules [11], laser mode switching [12], photoinduced isomerization of spiropyran chromophores [13], single photons using linear optical elements [14], information coded in hyperfine levels and processed by atom pairing through induced dipole–dipole interactions [15], carrier transmission controlled by magnetic fields [16], carbon nanotube transistors [17], carbon molecular switches [18], multimode interference waveguides of nonlinear material acting as phase shifters [19], etc. Biomolecules are successfully employed in optical logic simulation, as reported with bacteriorhodopsin [6, 7] and others [20, 21]. Very few studies were made on the binary logic encoding properties of chlorophyll, the common plant pigment, whereas efficient fabrication techniques are available for assembly and manipulation of molecular monolayers of chlorophyll a [22–24], theoretical explanations were reported on the absorption properties of total chlorophyll [25] and reverse saturable absorption of chlorophyll and its suitability as a sensitizer for photodynamic therapy were investigated [26]. In the present work, the wavelength-selective property and polarization sensitivity of total chlorophyll in the visible regime are demonstrated as a suitable medium for realizing optical Boolean logic at molecular level. Spectrophotometric studies are made with solutions of total chlorophyll and chromatographically isolated components, viz. chlorophyll a and b and carotenoids. The absorption characteristic with two absorption peaks and one transmission band are molecular properties and independent of concentration. The presence or absence of wavelengths corresponding to either one or both of the two characteristic absorption peaks can simulate optical logic input/output. Sensing the absorbance or transmittance, various logic functions like AND, OR and NOT can be realized at active-low or active-high conditions. Also, the shift in absorbance values for two different polarizations of monochromatic red light can simulate two logical states. However, the

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difference between the two logic states is not appreciably large.

2 Experimental results and discussion

For sample preparation, 5 g of fresh weight of pumpkin (Cucurbitaceae) leaves of different maturity stages, viz. juvenile (J), matured (M), semi-senescent (SS), i.e. partially turned yellow, and senescent (S), i.e. fully turned yellow, were separately kept dissolved in 100 ml of 80% acetone for 24 h in the dark. As the solutions of such high concentration yielded saturation in absorbance, those were taken as the starting solutions and assumed to be of 100% concentration. Solutions of further dilutions were prepared from the above. These solutions were expected to contain mixtures of chlorophyll varieties and carotenoids. Further isolation of pigments was done by thin-layer chromatography. Continuous variation of absorbance and transmittance over 400 to 700 nm with 0.7-nm resolution was measured with a Systronics 2202 dual-beam spectrophotometer. Emission spectra for different excitation wavelengths were measured with a Hitachi S4500 spectrofluorometer, scanning continuously with 0.2-nm resolution. Although the general spectral properties of plant chloroplastidial pigments are well known [27, 28], the present results are justified with the following studies.

Figure 1 represents the absorbance variation for different dilutions of total chlorophyll solution extracted from matured leaves. The concentrations of chlorophyll a and b were estimated by a standard method [29] recently upgraded [30]. Earlier studies [31] reported variation of absorption peaks and bandwidths with concentration at low temperature (298 to 77 K). However, the present results at room temperature indicate that the absorption peak wavelengths are molecular property of chlorophyll and remain fixed, independent of solution concentration. Also, the bandwidths, calculated with respect to absorption maxima at blue and red and minimum at green, remain almost constant within a certain concentration. The results are summarized in Table 1. The measurements were repeated by varying the temperature around room temperature (from 10 to 40 °C) keeping the samples within a thermocouple-controlled dry bath and essentially the same result was obtained.

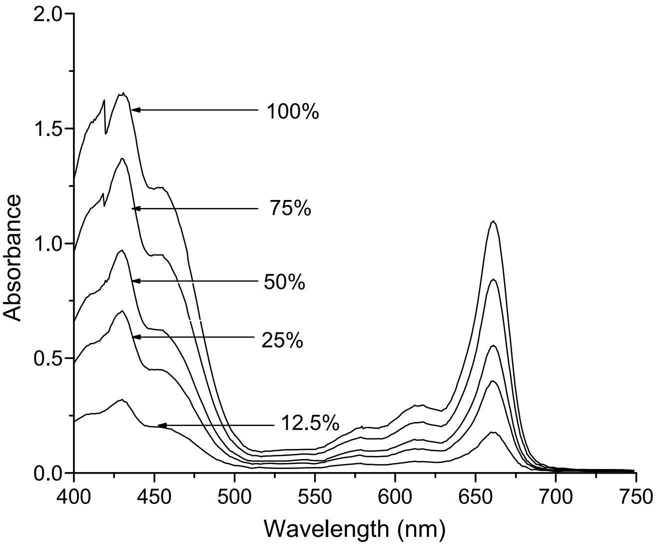

FIGURE 1 Absorbance–wavelength plot for different dilutions of total chlorophyll solution extracted from matured leaves

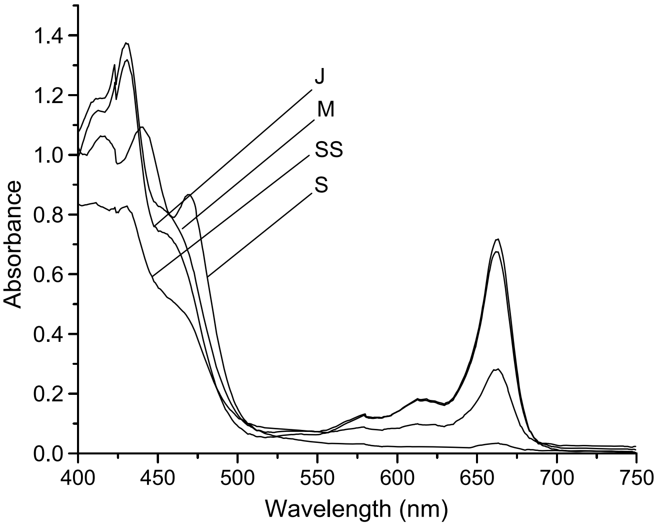

FIGURE 2 Absorbance–wavelength plot for chlorophyll solution of different maturity stages of leaves, viz. juvenile (J), matured (M), semi-senescent (SS) and senescent (S)

Figure 2 verifies the change in the above wavelength selectivity of chlorophyll with leaf maturity. On approaching senescence, the red absorbance is suppressed and the blue absorbance exhibits a red shift. To understand the behavior more systematically, artificial mixtures were prepared with different ratios of fresh and decomposed chlorophyll extracted from green and senescent leaves, respectively. The resultant absorbance variations are shown in Fig. 3, where a similar nature of the red shift of the blue absorbance and suppression of the red absorbance is noted. For the remaining part of the experiment, only matured chlorophyll was taken and the individual pigments were chromatographically isolated from that. As usual [27, 29], chlorophyll a exhibited absorbance peaks at around 430 (blue) and 663 nm (red), similar to total chlorophyll, chlorophyll b exhibited corresponding peaks at around 470 and 650 nm

Solution conc.	Pigment concentration (mg/l) chl-a	chl-b	Absorption/transmission bandwidth (nm) blue	green	red
100%	12.474	6.670	390.8–462.3	495.2–602.3	652.7–669.5
75%	9.636	4.927	400.7–445.5	492.4–633.8	652.7–669.5
50%	6.331	3.202	402.1–442.0	486.8–640.8	652.7–668.8
25%	4.531	2.306	402.8–441.3	482.6–645.7	652.7–668.8
12.5%	1.278	1.027	401.4–441.3	467.2–659.0	652.7–669.5

TABLE 1 Absorption and transmission bandwidths for different chlorophyll (a and b) concentrations

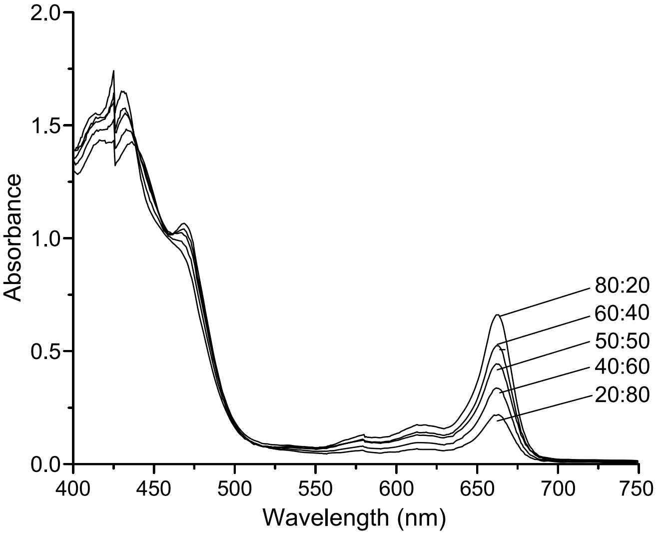

FIGURE 3 Absorbance–wavelength plot for artificial mixtures of fresh and decomposed chlorophyll solutions at different ratios indicated against the curves

and carotenoids (β-carotene and xanthophylls) had no red peak.

The intensity of chlorophyll fluorescence emission in the red region [32] is very small, only a few percent of the incident intensity. The possibility of disturbing the red absorbance is supposed to be minimum. However, the fluorescence emission for total chlorophyll and chromatographically isolated pigments were measured for different excitation wavelengths as summarized in Table 2. For total chlorophyll, the fluorescence peak occurred at around 473 nm for excitation wavelengths up to 450 nm, i.e. the blue region. On increasing the excitation wavelength to 500 nm, the peak shifted to 651 nm and became much suppressed. Thus, the fluorescence was always well separated from the absorption peak. For chlorophyll a, no significant emission peak occurred below 450-nm excitation wavelength. For excitation at 460–500 nm, a feeble peak occurred at around 653 nm. For chlorophyll b, small peaks occurred for excitation wavelengths less than 450 nm. For higher excitation wavelengths, no significant fluorescence was found. Carotenoids exhibited no red fluorescence at all.

Total chlorophyll, for the present study, is thus grossly characterized with two distinct absorption bands at blue (402–441 nm) and red (653–669 nm) and one transmission band at green and yellow (483–646 nm). The main purpose of the present work is to employ these properties to generate optical logic. However, a qualitative explanation at molecular level for the origin of switching of electrons between states and resultant absorption is being presented with the popular ‘particle in a box’ model.

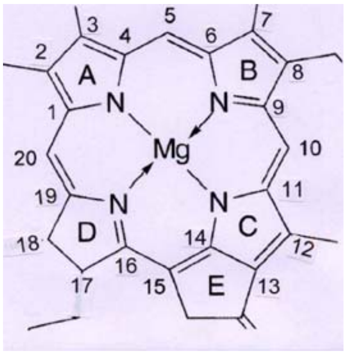

FIGURE 4 Simplified diagram of porphyrin ring of chlorophyll molecule [33, 34]

The porphyrin structure, as shown in Fig. 4, is common to all chlorophylls, while the side chains are different [33, 34]. The property of two absorption peaks is characteristic to all the chlorophylls, although the peak positions are different from one another [27–29]. Thus, the origin lies in the basic porphyrin structure consisting of conjugated bonds. Electrons following the path of conjugated bonds are switched between energy levels when the total length (L) of the cyclic path of conjugation becomes a multiple of the wavelength (λ). The lowest energy is that required for switching from the highest filled molecular orbital to the lowest unoccupied molecular orbital, so that

$$\lambda = 8mL^2c/[(n+1)h]\,, \tag{1}$$

the symbols having the usual meaning. Three different possible paths of the cyclic conjugated bond are defined, as given below, for the calculation of L. The carbon atoms are numbered in Fig. 4 starting from pentagon A.

Path 1: atoms C_1 to C_{20} and back to C_1 via pentagons A, B, C and D with intermediate hexagons. A total of 20 atoms are involved.

Path 2: pentagon E is also involved; a total of 21 carbon atoms.

Path 3: atoms C_1 to C_6, C_6 to N, N to C_9, C_9 to C_{16}, C_{16} to N, N to C_{19}, C_{19} to C_{20} and back to C_1. A total of 16 atoms are involved.

Assuming the limits for the C–C bond length to be 0.120 to 0.154 nm and the C–N bond length to be 0.147 to 0.210 nm, the L values are calculated for the above three paths and the corresponding wavelength ranges are calculated using (1) as shown in Table 3. The wavelength values are not similar to

Sample	Excitation wavelength (nm)									
	410	420	430	440	450	460	470	480	490	500
Total chlorophyll	673 0.79	672 0.88	673 1.0	672 0.8	671 0.28	651 0.54	651 0.43	651 0.2	653 0.08	653 0.13
Chlorophyll a	666 0.08	663 0.10	660 0.14	654 0.15	652 0.23	653 0.33	651 0.25	651 0.1	650 0.03	–
Chlorophyll b	669 0.37	668 0.4	668 0.52	668 0.35	668 0.08	–	–	–	–	–

TABLE 2 Fluorescence emission wavelengths (nm) and corresponding normalized amplitudes for chloroplastidial pigments at different excitation wavelengths

Path	C–C bond length (nm)	C–N bond length (nm)	L (nm)	λ (nm)	λ (nm) assuming $L = L/\sqrt{2}$
Path 1	0.120	–	2.40	903	452
	0.154	–	3.08	1488	744
Path 2	0.120	–	2.52	951	475
	0.154	–	3.234	1566	783
Path 3	0.120	0.147	2.268	997	498
	0.120	0.210	2.520	1230	615
	0.154	0.147	2.744	1459	729
	0.154	0.210	2.996	1739	869

TABLE 3 Calculation of absorption wavelengths (λ) corresponding to possible paths of conjugation (L)

the blue and red wavelengths. However, careful inspection reveals that these values are in a certain proportion. If each value of L is reduced by $\sqrt{2}$ times, the λ values come out to be in good agreement with the blue and red wavelengths, as shown in Table 3. The above explanation is thus a schematic interpretation of the absorption wavelengths. The effective distance between the atoms may change depending on bond angle. Also, the actual molecular orientation is three dimensional. The exact determination of the path length is thus complicated and beyond the scope of the present work.

The schemes for simulating optical logic operations are now outlined below.

Two-input AND operation

Visible light of two different wavelengths is considered to be the inputs to the gate. If both of the inputs are either red or blue, absorption is high. If either one is absent and replaced by another wavelength of the transmission band, e.g. green or yellow, absorption is low. At the input, the presence of blue or red is assigned ‘1’. At the output, high absorbance means ‘1’ (active-high operation). The conditions are mentioned in Table 4.

The above scheme was experimentally verified with different concentrations of chlorophyll solution using the following setup. Three LEDs of different colors, viz. blue, green and red (wavelength ranges for uniform illumination indicated in Table 4), with equalized intensity were kept close together in front of a quartz container of 1-cm inner width filled with chlorophyll solution. A selenium detector (analogous to human eye response to visible wavelengths) calibrated in lux was placed on the other side. The required inputs were generated by switching on/off the LEDs. The normalized outputs with respect to the maximum value are shown in Table 4. It is apparent that when green is off, the theoretical truth table is followed and, when it is on, the presence of wavelengths other than blue or red is reflected at the output.

Two-input OR operation

The same absorbance characteristics can be treated in another way. Now, at the input, the absence of blue/red is assigned ‘1’. At the output, low absorbance means ‘1’ (active-low operation). The conditions are summarized in Table 4.

NOT operation

This can be simulated with the transmittance instead of absorbance. The presence or absence of the pass (green plus yel-

Two-input AND operation:

Input/output conditions			Truth table			Experimental verification					
						LEDs			Normalized output		
A (blue)	B (red)	Output absorb.	A	B	Y	blue	red	green	100%	50%	25%
Absent	Absent	Low	0	0	0	OFF	OFF	OFF	0.0	0.0	0.0
						OFF	OFF	ON	0.74	0.74	0.82
Absent	Present	Low	0	1	0	OFF	ON	OFF	0.19	0.31	0.36
						OFF	ON	ON	1.0	0.91	0.92
Present	Absent	Low	1	0	0	ON	OFF	OFF	0.13	0.20	0.28
						ON	OFF	ON	0.87	0.91	0.90
Present	Present	High	1	1	1	ON	ON	OFF	0.35	0.5	0.61
						ON	ON	ON	0.95	1.0	1.0
Two-input OR operation:											
Present	Present	High	0	0	0	ON	ON	OFF	0.35	0.5	0.61
						ON	ON	ON	0.95	1.0	1.0
Present	Absent	Low	0	1	1	ON	OFF	OFF	0.13	0.2	0.28
						ON	OFF	ON	0.87	0.91	0.90
Absent	Present	Low	1	0	1	OFF	ON	OFF	0.19	0.31	0.36
						OFF	ON	ON	1.0	0.91	0.92
Absent	Absent	Low	1	1	1	OFF	OFF	OFF	0.0	0.0	0.0
						OFF	OFF	ON	0.74	0.74	0.82

TABLE 4 Realization of AND and OR operations with absorption properties. The wavelength ranges of uniform illumination for the three LEDs are: red 613–678 nm, blue 434–477 and 495–529 nm, green 536–545, 559–567 and 574–590 nm

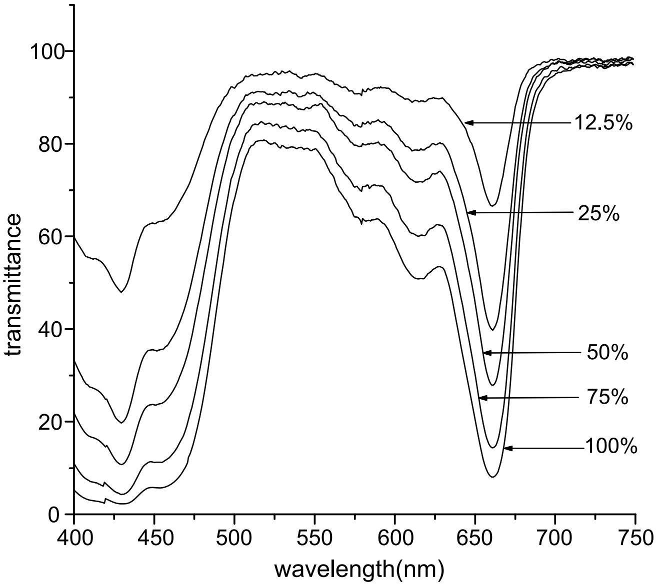

FIGURE 5 Transmittance–wavelength plot for different dilutions of total chlorophyll solution extracted from matured leaves

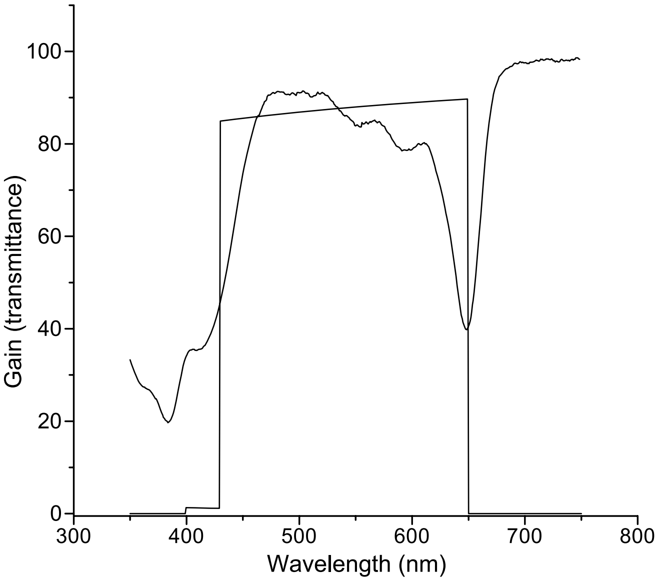

FIGURE 6 Comparison of transmittance–wavelength plots of chlorophyll with band-pass filter generated for low-pass gain $= 1/[(\lambda/s)^2 + 1.414(\lambda/s) + 1]$, with $4 < \lambda < 4.3$, and high-pass gain $= 1/[(s/\lambda)^2 + 1.414(s/\lambda) + 1]$, with $4.3 < \lambda < 6.5$

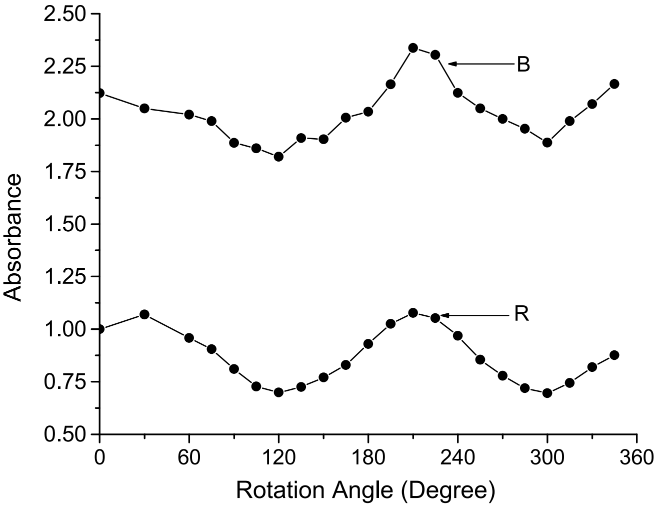

FIGURE 7 Cyclic change in chlorophyll absorbance with polarization varied through 360° with respect to an arbitrary starting point for both red (R) and blue (B) peaks

low) band determines this operation. The transmission characteristics for different concentrations are shown in Fig. 5. The sharp depressions at around 430 nm and 663 nm and the flat response in between resemble a band-pass filter as outlined in Fig. 6 with standard formulae.

The shift in absorbance values for two different polarizations of the same monochromatic light can simulate two logical states with a single wavelength. The polarization sensitivity of chlorophyll was investigated with a slight modification in the instrumental setup of the spectrophotometer. Two matched polarizers were inserted, one in each path of the two light beams, the planes of polarization being parallel. Both were rotated through equal angles up to 360°. Correspondingly, a cyclic change in absorbance was noted for both red and blue peaks as shown in Fig. 7 with respect to an arbitrary starting point. For the intermediate wavelength range of 440–480 nm, the absorbance remained almost invariant with polarization. It may be mentioned that the difference in absorbance at red and blue peaks of the reflection spectra of chlorophyll a for two different polarizations was reported earlier [22], although the difference was very small. The present results also yield a small difference, the maximum being within $\sqrt{2}$ times the minimum. However, the variation is distinct and more systematic for the red (Fig. 7), where the absorption band is very sharp (Table 1). Therefore, red monochromatic light with polarizations apart by 90°, corresponding to maximum and minimum absorption, respectively, may be treated as the two logical states.

3 Conclusions

It was demonstrated that the absorption features of chlorophyll in the visible-wavelength range with two absorbance peaks and one transmission band, which are molecular properties and are invariant with concentration, can be employed to simulate all-optical Boolean logical operations. The polarization sensitivity at the red wavelength is another means of simulating binary states with a single wavelength.

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