

Synthesis and photoelectrical properties of carbon nanotube–dendritic porphyrin light harvesting molecule systems

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Abstract

Supramolecular structures consisting of dendritic porphyrins and single-walled carbon nanotubes (SWNTs) have been prepared and characterized as an efficient donor/acceptor system. Non-covalent interactions enable the pair system to produce suitable electron transfer through a process occurring from the dendritic porphyrin core to the graphenic wall of carbon nanotubes. The role of structure/architecture of our dendritic molecules on SWNT photoelectrical behaviour has been also investigated.

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1. Introduction

Recently, functionalization of carbon nanotubes through surface modification has attracted relevant interest [1–4]. Functionalization strategies involving reactions of organic or polymeric molecules onto carbon nanotubes have been primarily focused on dispersion or dissolution properties. In particular, non-covalent interactions of porphyrins with single-walled carbon nanotubes (SWNTs) have been used for the dispersion and also for the separation of semiconducting and metallic tubes [5–9]. A donor/acceptor system consisting of an anionically-functionalized porphyrin and a cationically-functionalized pyrene stacked on SWNTs has been shown to exhibit electron transfer properties [10].

Non-covalent modifications involving dyes have used polymers, such as poly-*m*-phenylenevinylene [11] and dendrimeric polyamidoamine (PAMAM[®]) [12,13], and molecules with an extended π -system, such as poly(aryleneethynylene) [14], anthracene [15], phthalocyanine [16] and porphyrin

[17]. The use of organic dyes, as porphyrins, enables the use of photovoltaic devices for visible light applications [18,19] and photoresponsive devices [20]. Porphyrin assemblies are of great relevance as models for the study of energy and electron transfer as light harvesting antennae in the photosynthetic reaction centre [21].

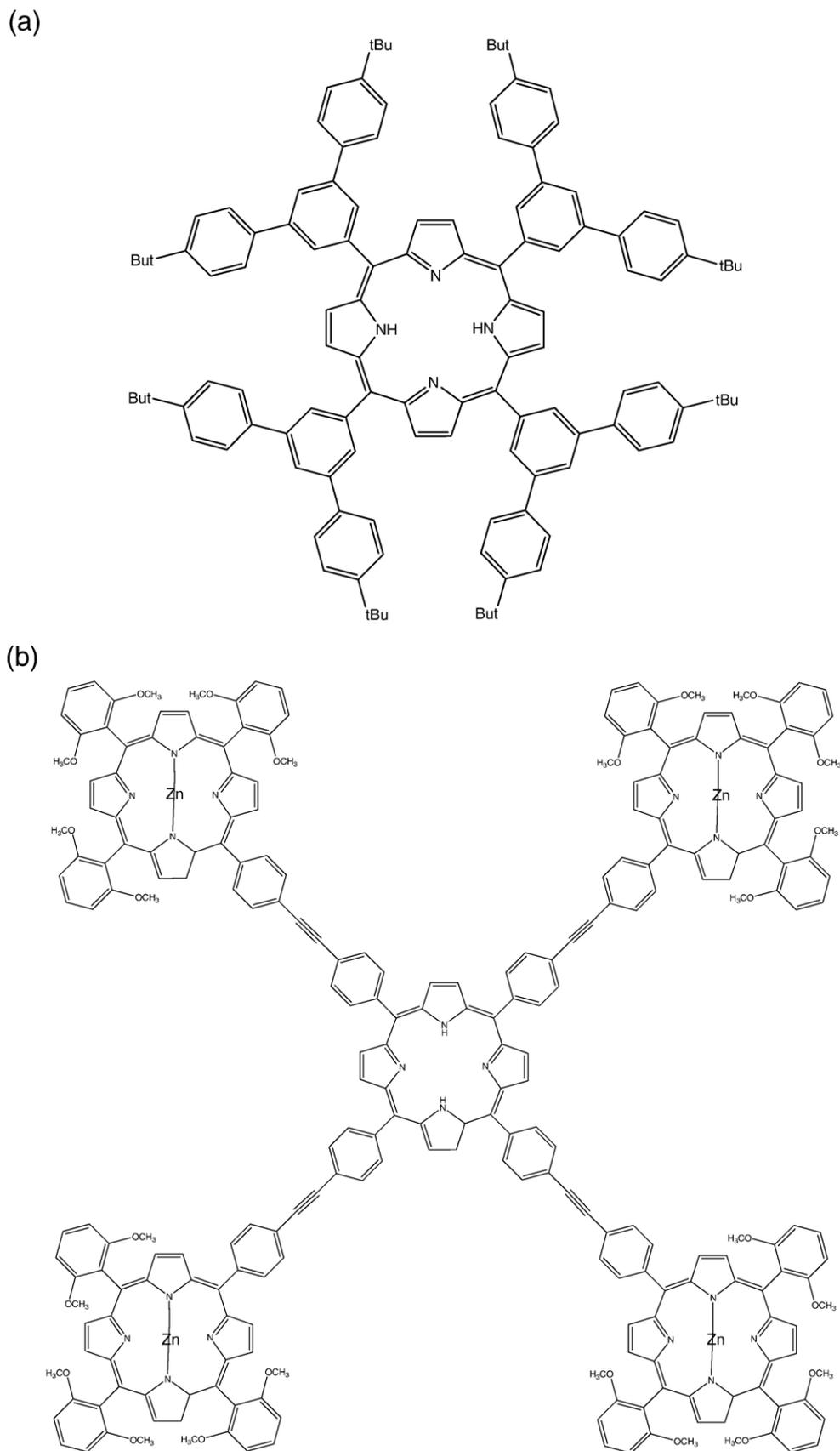
More recently, incorporation of antenna molecules, such as dendritic porphyrins, that are able to absorb light and channel it to a reaction core interacting with the extended π electrons of carbon nanotubes would constitute an ideal supramolecular nano-assembly for potential photovoltaic applications [22,23].

In the present paper, we have explored the possibility of combining SWNTs with two dendritic porphyrins characterized by a different structure/architecture, with the aim of evaluating the influence of the latter parameters on the photoelectrical answer of SWNTs non-covalently interacting with the porphyrins. The highly aromatic structure of porphyrins ensures the high level of π -bonds needed to interact non-covalently with carbon nanotubes. The different architecture and rigidity of the two porphyrin structures allow to differentiate the extent of interactions between the porphyrin and carbon nanotube.

The first structure used as light harvesting antenna molecule is 1,3,5-phenylene-based dendritic porphyrin, having a pyrrole

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core and peripheral phenylene groups. Presumably, the non-covalent interaction mostly occurs between the pyrrole core of porphyrin and the graphenic wall of carbon nanotubes. In addition, also the peripheral phenylene groups may play a relevant role in non-covalent interactions with SWNTs, as they make the porphyrin structure more flexible, thus favouring the intimate contact with the surface of SWNTs.

On the basis of the above non-covalent interactions, a second light harvesting antenna molecule was prepared and evaluated, being characterized by a star-like array of five porphyrins. Indeed, this latter molecule is a dendritic porphyrinic pentamer made of four peripheral porphyrins as chromophores, which absorb the light and channel it by excitement energy to the central trapping porphyrin. The trap, characterized by a highly aromatic structure, non-covalently interacts with the graphenic walls of carbon nanotubes transferring energy to them. This molecule is expected to have better light harvesting properties because of the highly conjugated structure.

In this paper, we report the photoelectrical properties of the two aforementioned dendritic molecules. Such molecules display an excellent π -conjugation and, in combination with photoexcited electron acceptors such as nanotubes, are expected to be beneficial for testing new paradigms in charge transfer management.

2. Experimental details

SWNTs were obtained from CarboLex, Inc. and consisted of ≈ 50 –70 vol.% carbon as SWNTs, produced using the arc discharge method with a Ni–Y catalyst. Their characteristic diameter was in the range of 1.3–1.5 nm and most of them were embedded in bundles with a typical size of 7–12 nm.

The two dendritic porphyrins with light harvesting properties used are: i) 1,3,5-phenylene-based dendritic porphyrin (D-porphyrin 1), shown in Fig. 1(a), synthesized following the Kimura et al. method [24], and ii) a dendritic porphyrinic pentamer (D-porphyrin 2), shown in Fig. 1(b), synthesized following the Prathapan et al. method [25].

DMF (Aldrich) was used without further purification as the solvent of D-porphyrins and as SWNT dispersant in order to prepare SWNT/porphyrin blends.

Non-covalent interactions between porphyrins and SWNTs were optimized by sonicating together the two components of the pair in DMF (1 mg/1 ml) for 2 h. After centrifugation in order to remove undissolved SWNTs, the clear solution was analyzed and used. For comparison, a sample of pristine nanotubes and a sample of porphyrin were sonicated alone for 2 h in the same solvent.

TEM analysis of the samples was performed with a Jeol Jem 2010 microscope. The TEM images were obtained from the DMF solution of porphyrin/SWNT pair and from the DMF suspension of pristine SWNTs, placed on a carbon-coated copper grid and allowed to dry in vacuum (10^{-1} Pa) for 12 h.

^1H NMR analysis of the samples was performed with a Varian Gemini 300. A Perkin-Elmer Lambda 9 UV spectrophotometer was used to monitor possible modifications of porphyrin absorption spectra as a consequence of the interac-

tions with carbon nanotubes. Spectra were measured on a DMF solution of porphyrin-modified SWNTs and on a DMF solution of the neat porphyrins.

Samples for the photoelectrical study were prepared by depositing a drop (0.4 μl) of the solution of D-porphyrin 1 and 2 that were left to evaporate onto platinum patterned electrodes (electrode distance 3 μm) set on a $\text{Si}_3\text{N}_4/\text{Si}$ substrate. Photoelectrical measurements were obtained on the films for several on/off light illumination cycles. The conductivity of the films was monitored as a function of exposure time through a solar simulator, under Xenon lamp with an input power of $130 \text{ mW} \cdot \text{cm}^{-2}$.

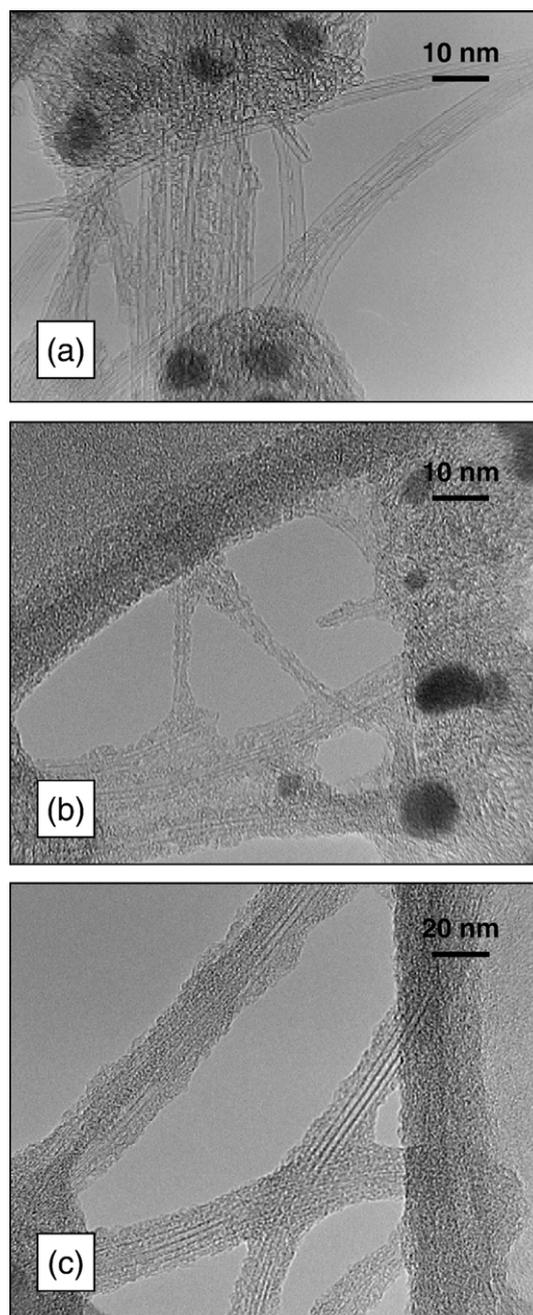


Fig. 2. TEM micrograph of (a) pristine SWNTs, and (b) D-porphyrin 1 coating SWNTs, (c) D-porphyrin 2 coating SWNTs.

For the dark conductivity measurements, a Keithley 4200 source measuring unit was used for taking the I – V characteristics.

The transport properties were measured in a thin-film transistor geometry. The transistor geometry was previously reported [13]. Briefly, doped silicon wafers that had 250 nm of thermally grown SiO_2 on their surface were used. Source and drain electrodes (40 nm of Al followed by 40 nm of Au) separated by 8 μm were deposited through e-beam lithography.

We measured the source–drain current (I_{DS}) as a function of the gate voltage (V_{G}) under gate voltage sweep maintaining the drain voltage fixed at 0.2 V.

3. Results and discussion

The first qualitative evidence of a sort of non-covalent interaction between the porphyrin molecules and SWNTs has been given by the partial solubilization of carbon nanotubes after sonication in DMF when in presence of porphyrin. After centrifugation, the black solution obtained remained stable even after several weeks.

TEM microscopy (Fig. 2) allowed to confirm the above result showing an intimate interaction between the two porphyrins and carbon nanotubes. In fact, Fig. 2a shows the clean sidewalls of pristine nanotubes, while a relevant porphyrin adsorption on SWNT sidewalls, responsible of their coating, is evident in Fig. 2b and c. These latter panels refer to TEM

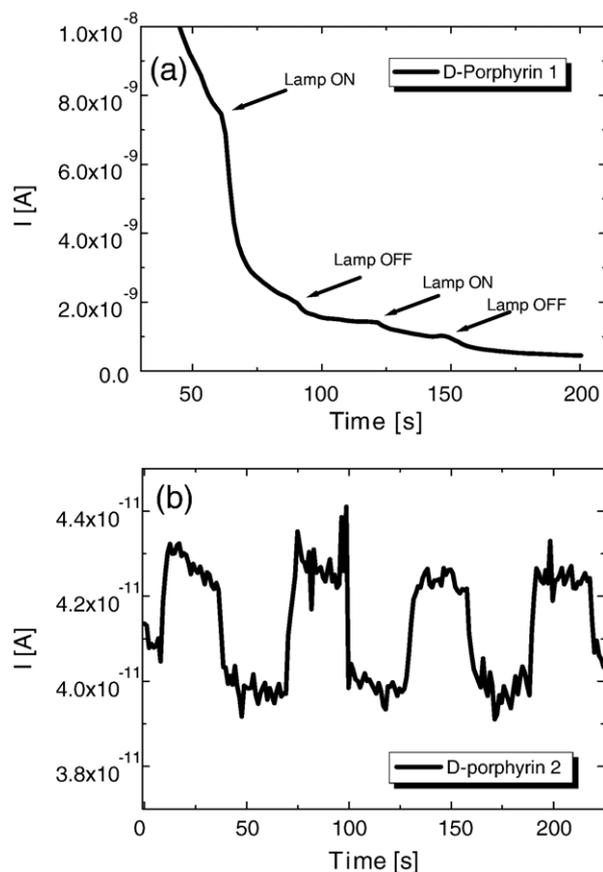


Fig. 3. Evolution of the (a) D-porphyrin 1 and (b) D-porphyrin 2 film currents under light-on and light-off steps in air.

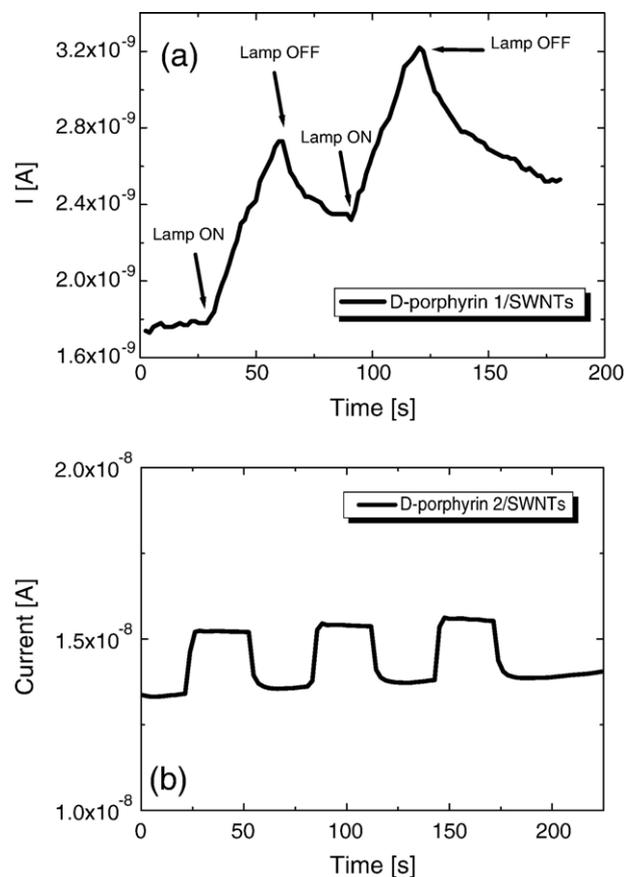


Fig. 4. Evolution of the (a) D-porphyrin 1/SWNTs and (b) D-porphyrin 2/SWNTs film currents under light-on and light-off steps in air.

magnifications of D-porphyrin 1 and D-porphyrin 2, respectively. Besides providing a clear evidence of the solubilization effect mentioned above, TEM characterization suggests that the two porphyrins interact non-covalently with carbon nanotube walls thanks to their highly aromatic structure.

In order to confirm this hypothesis, NMR analysis was performed. ^1H NMR spectrum of D-porphyrin 1 shows only a broadening of signals in the presence of carbon nanotubes. Although, it is not detectable a shift of the typical signals of the molecule, presumably the broadening of the signals could suggest a possible non-covalent interaction between the dendritic molecule and carbon nanotubes, as confirmed in the literature [12,26]. This possible interaction is, however, weak. Also, in the case of D-porphyrin 2, ^1H NMR signals of pristine molecule do not change in the presence of carbon nanotubes and broadening is lower.

Concluding, NMR analysis shows only a broadening of signals of D-porphyrins due to their change of electric field in the presence of carbon nanotubes.

UV–Visible and Raman analyses do not show remarkable shifts in the signals characteristic of D-porphyrins in the presence of SWNTs.

The typical photoelectrical response of D-porphyrin 1 and D-porphyrin 2 in thin films for the on/off light illumination cycles in air is shown in Fig. 3. The main feature in the photoelectrical temporal behaviour is an increase of the resistance under the illumination steps for the D-porphyrin 1 (Fig. 3a) while

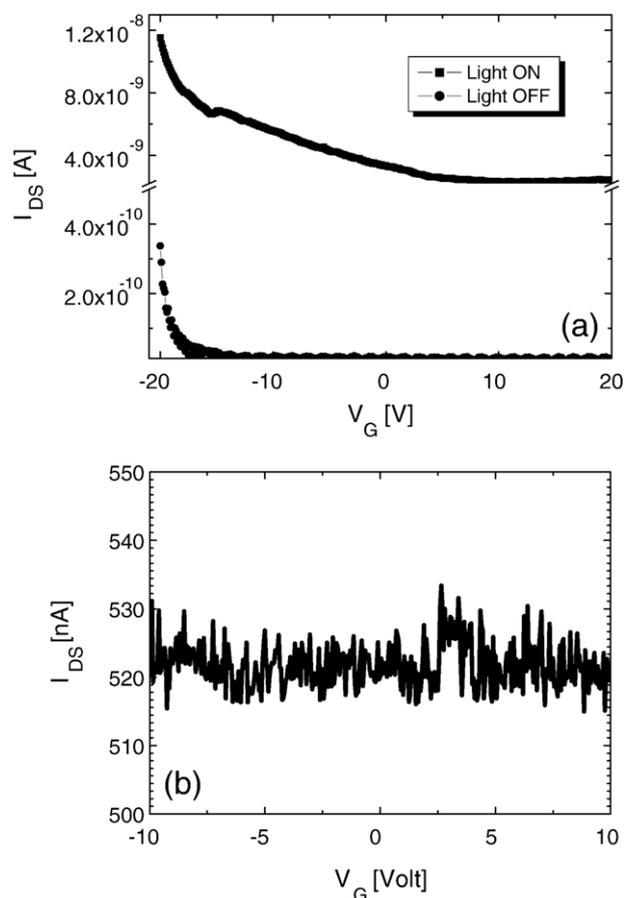


Fig. 5. (a) Transfer curve of the D-porphyrin 2/SWNTs device before and after illumination. Light was left on for 30 s. The curve under illumination shows ≈ 10 V shift of the transfer curve toward positive gate voltages. (b) I_{DS} as a function of V_G for pristine SWNTs.

a reversible rise/decay of the photocurrent in response to the on/off illumination step for D-porphyrin 2 (Fig. 3b) was observed. Moreover it is evident that the photoelectrical response measured for the D-porphyrin 2 shows an evident photocurrent stability when exposed to several on/off cycles while in the case of D-porphyrin 1 any photocurrent signal was recorded after the first cycle.

The currents of D-porphyrin 1/SWNTs and those of D-porphyrin 2/SWNTs systems were then monitored as a function of the time as the light is on/off switched. An analysis of the diagrams reported in Fig. 4 shows that changes of the conductivity under illumination of the D-porphyrin 1/SWNTs (Fig. 4a) are reverse and higher than those of the neat molecule.

Moreover, the difference between the conductivity as well as the photoresponse of the D-porphyrin 2/SWNTs system (Fig. 4b) and the other system is that the on and off currents increased, with the dark current of D-porphyrin 2/SWNTs that is much higher than that of D-porphyrin 1/SWNTs.

Fig. 5 shows the transfer curve of the transistor device fabricated with D-porphyrin 2/SWNTs in the dark and under illumination. When illuminated the device shows a shift of the threshold voltage toward positive voltages; this finding is consistent with a hole doping of the SWNTs as reported elsewhere [28]. According to the data reported in Ref. [28], this result means

that under illumination we observe an electron transfer from the SWNTs to the porphyrin as observed in Fig. 4b where the photocurrent signal is completely reversible. Even if the porphyrins are considered electron donors [22,27], by comparing the transfer curves in Fig. 5a and b between SWNTs and D-porphyrin 2/SWNTs system it is evident that there was a transfer of electrons to the SWNTs upon addition of porphyrin and under illumination of the compound, some of the electrons that have been transferred to the SWNT are transferred back to the porphyrin molecule in the excited state [28]. Moreover the recovery of the photoresponse indicates that the porphyrin molecule remains an electron donor in the excited state.

4. Conclusions

We have prepared carbon nanotube–dendritic porphyrin light harvesting molecule systems exploiting the versatility of the dendritic macromolecule on the dissolution properties through the interactions of conjugated systems. This study shows that dendritic molecules can be used to improve the photoelectrical response of single-walled carbon nanotube based devices accomplishing a task similar to biological processes where light is sensed and converted into a signal. In principle, the approach of mixing and matching organic and inorganic materials will be fundamental for the design of specific molecular structures that could be varied through chemical synthesis, making a variety of devices that detect and respond to specific wavelengths of light.

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