Optimal Sunlight Harvesting in Photovoltaics and Photosynthesis

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ABSTRACT: Materials employed to harvest sunlight are commonly recognized to be at a premium when their optical absorption peaks in the visible, extends to the infrared, is panchromatic, and is matched to the solar spectrum. By contrast, natural photosynthetic absorbers such as chlorophylls and carotenoids display absorption spectra with narrow peaks for yet-unknown evolutionary reasons. Beyond such general observations, a rigorous treatment of sunlight harvesting optimization is still lacking. In this work, we provide a quantitative analysis of optimal solar energy harvesting in materials. We derive optimal absorption spectra as a function of absorber thickness, elucidate the concept of solar-matched absorption and its applicability limits, and define a procedure to rank photovoltaic materials for sunlight harvesting. In addition, we suggest a possible explanation for why absorption in plant photosynthetic pigments occurs in narrow energy windows.



Photovoltaics (PV) and natural/artificial photosynthesis aim at converting sunlight to electricity or chemical fuels.¹⁻⁷ In all these technologies, the first microscopic process leading to energy conversion and storage is sunlight absorption in a semiconductor. Absorption of light at visible and infrared (IR) photon energies in the 0.3-4 eV range typical of solar radiation varies significantly among different classes of semiconducting materials. The different nature of the electronic states in inorganic crystals and molecular materials determines key differences in their absorption spectra. For example, inorganic semiconductors typically present wide absorption features above the energy gap due to transitions between delocalized valence and conduction band states, while conjugated small molecules and polymers possess localized excitonic states and consequently narrower absorption peaks (broadened by vibronic effects) that can be hard to extend to the full spectrum.8

Optimizing materials for sunlight absorption is at the center of significant research efforts. The trivial solution of employing materials as thick as needed for quantitative sunlight harvesting is not viable in almost all practical situations; a trade-off is often necessary between the thickness of the sunlight absorber and the diffusion length of carriers and excitons involved in the energy conversion process. For this reason, it is common in systems employing molecular absorbers to harvest a fraction of sunlight well below unity even at peak absorption energies. This situation is found, among other systems, in solid-state solar cells based on polymers,⁹ small molecules or quantum dots,^{3,10} dyesensitized solar cells,^{11,12} and photosynthetic antenna complexes.^{13,14} Given that the overall absorption strength for a fixed thickness of a material is regulated by optical sum rules, the key variable to be optimized is the *shape* of the absorption spectrum rather than its absolute strength. At present, there is little quantitative understanding of the optimal shape of the absorption spectra of sunlight harvesting materials. Yet, qualitative statements regarding desirable features are common in the literature, including the need for high peak absorption values, broad absorption spectra extending to IR or ultraviolet (UV) photon energies, or absorption matched to the incident solar spectrum.^{9,10,15–19} In particular, solar-matched absorption (SMA), namely, the resemblance of a material's absorption spectrum with the incident solar flux distribution, is a commonly employed paradigm for effective sunlight harvesting in materials.^{9,15,16,18} Yet, despite its frequent use in the literature, the SMA concept is not quantitatively defined and lacks predictive character as well as a formal justification for why it should be considered as a reliable sunlight absorption figure of merit.

A related fact is that chlorophylls and other pigments found in natural photosynthetic organisms show narrow absorption peaks, in stark contrast with the SMA tenet.^{4,13} It seems reasonable that natural photosynthetic systems would optimize a variety of aspects related to sunlight conversion rather than merely maximizing the amount of absorbed sunlight as in PV. An analysis of the absorption spectra of natural photosynthetic pigments may thus offer insight about the advantages of absorbing sunlight in narrow energy ranges. This scenario is intriguing and stimulates the search for a common framework to investigate optimal absorption strategies in artificial and natural solar energy absorbers. A quantitative treatment may allow us to design optimal sunlight absorbers and unravel the mystery behind the use of narrow absorption peaks in natural systems.

Received:September 10, 2013Revised:November 13, 2013Published:November 14, 2013



The Journal of Physical Chemistry C

In this work, we derive optimal absorption spectra of materials for sunlight harvesting as a function of absorber thickness. Our calculations demonstrate that SMA maximizes sunlight capture only at small and intermediate thicknesses, as derived under specific assumptions. For different thicknesses of the absorber material, we derive optimal absorption spectra analytically and confirm our results numerically. We further define a quantitative figure of merit for SMA and use experimental absorption data from the literature to compute the proposed figure of merit and show that it can successfully rank materials employed in PV for sunlight absorption. Taken together, our treatment both expands the scope and exposes some shortcomings of the widely employed SMA concept. Our analysis further shows that chlorophyll photosynthetic pigments can be ranked as poor sunlight absorbers. We find however that an advantage of their nonoptimal absorption is an increased robustness in photon collection with respect to variations of incident sunlight intensity and changes in the number of absorbing pigments. This scenario suggests a possible explanation behind the narrow absorption bands of chlorophylls, namely, that plants may be optimized for robust (as opposed to maximal) sunlight absorption.

THEORY

Knowledge of the optical absorption spectrum $\alpha(E)$ (units of inverse length) for photon energies *E* in the 0.3–4 eV range typical of sunlight allows one to quantify the performance of a material for solar energy harvesting. The absorbed photon flux $J_{\rm abs}$ for a flat film of thickness *L* of a material with optical gap $E_{\rm g}$ and for a single light pass can be computed as

$$J_{abs}[\alpha](L) = \int_{E_g}^{\infty} J_{ph}(E) \cdot [1 - e^{-\alpha(E)L}] dE$$
(1)

where $J_{\rm ph}(E)$ is the AM1.5 solar energy flux, in units of photons s⁻¹ m⁻² eV⁻¹, obtained here from ref 20 and shown in Figure 1a. The square bracket on the left-hand side of eq 1 highlights the fact that $J_{\rm abs}$ is a functional of the absorption spectrum $\alpha(E)$.

It is often advocated, although without formal justification, that the optimal absorption α_{opt} optimizing J_{abs} in eq 1 is "solarmatched", in the sense that $\alpha_{opt}(E) \propto J_{ph}(E)$.²¹ This rule of thumb can be loosely justified by the fact that if the absorption coefficient $\alpha(E)$ and the incident sunlight flux $J_{ph}(E)$ have a similar behavior, the fraction of absorbed sunlight (also called absorbance) $A(E) = 1 - e^{-\alpha(E)L}$ in eq 1 will be high at energies where the photon flux $J_{ph}(E)$ is high, thus resulting in an optimal current J_{abs} for the considered thickness. Our analysis below elucidates the origin of this SMA rule of thumb and its applicability limits.

At the outset, we remark that a simple optimization of the functional J_{abs} in eq 1 leads to the unphysical solution $\alpha(E) \rightarrow \infty$, thus showing that a meaningful discussion of optimal absorption requires a constrained optimization of J_{abs} . It must be in the spirit of such a constrained optimization that the SMA spectrum α_{smar} or any other absorption spectrum, can be considered optimal. A possible constraint to be imposed stems naturally from the *f* sum rule of optics,²² stating that the integral of the absorption spectrum over the energy range significant for electronic transitions is a constant depending only on the electron density of the system.



Figure 1. (a) The AM1.5 incident solar spectrum from ref 20 showing a maximum photon flux at $E_{max} \approx 0.8$ eV. (b) The four optimal absorption spectra derived analytically for different thickness ranges. All four spectra are normalized to the same integral *I*. The delta-like spectrum employed here possesses a 10 meV width. It reaches much higher values than shown in the figure, as indicated by the arrow.

Here, in comparing absorption spectra, a constant value of I is imposed for the integral of the absorption spectra over the sunlight energy range of 0.3-4 eV

$$\int_{0.3\,\mathrm{eV}}^{4\,\mathrm{eV}} \alpha(E) \,\mathrm{d}E = I \tag{2}$$

With this approach, the quantity to be optimized is not the absorption strength but rather the shape of the optimal absorption spectrum $\alpha(E)$ for a constant integrated absorption *I*. An additional constraint to impose is $\alpha(E) \ge 0$ at all photon energies *E* because the absorbing medium has no optical gain under sunlight illumination.

We emphasize that the optimal absorption $\alpha_{opt}(E,L)$ maximizing J_{abs} in eq 1 under the constraint in eq 2 depends on the thickness L of the absorber. While it is commonly thought that there is an "absolute best" absorption spectrum for a solar harvesting material, the mathematical formulation of the problem suggests instead that the optimal absorption spectrum depends on the thickness of the absorber. In this context, the thickness is best expressed in units of the absorption depth L_D = $\alpha^{-1}(E)$, defined as the depth inside of the material where sunlight intensity at energy E decreases to 1/e of its incident value (see eq 1). The reduced thickness $\alpha L = L/L_D$, also known as the optical thickness, expresses the thickness of the absorber in units of optical depth. We derive below four different solutions corresponding to different thickness values covering all regimes of practical interest.

Case 1: Very Small Thickness. For very small optical thicknesses $\alpha L \rightarrow 0$, the absorbed photon current J_{abs} becomes linear in the thickness L (as seen by Taylor-expanding the exponential in eq 1), and the slope $\partial J_{abs}/\partial L$ is given by the overlap integral of the incident photon flux and absorption spectrum

$$\lim_{aL \to 0} \frac{\partial J_{abs}}{\partial L} = \int_{E_g}^{\infty} J_{ph}(E) \alpha(E) \, dE$$
(3)

Because J_{abs} vanishes for L = 0 and is linear for $L \rightarrow 0$, the absorption spectrum α_{opt} maximizing the integral on the righthand side of eq 3, representing the slope of J_{abs} versus L for very small thicknesses, also maximizes J_{abs} and thus guarantees optimal sunlight harvesting at very small thicknesses.

As shown below, a formal solution for the optimal absorption spectrum at such a very small thickness regime is given by a delta function centered at the energy E_{max} for which J_{ph} is maximal. Combining this fact with the constraint in eq 2, we obtain

$$\alpha_{\rm opt}(E, \, \alpha L \to 0) = I \cdot \delta(E - E_{\rm max})$$
 (4)

We can prove this result by substituting $\alpha_{opt}(E, \alpha L \rightarrow 0)$ on the right-hand side of eq 3

$$\int_{E_g}^{\infty} J_{\rm ph}(E) \alpha_{\rm opt}(E) \, \mathrm{d}E = I \cdot J_{\rm ph}(E_{\rm max})$$

and showing that this integral is larger than $\int_{E_g}^{\infty} J_{ph}(E)\alpha(E) dE$ for any other absorption spectrum $\alpha(E)$ satisfying the constraint in eq 2.

In other words, we want to prove that

$$I \cdot J_{\rm ph}(E_{\rm max}) \ge \int_{E_g}^{\infty} J_{\rm ph}(E) \alpha(E) \, \mathrm{d}E \tag{5}$$

We use the definition of the Riemann integral to rewrite this inequality as

$$J_{\rm ph}(E_{\rm max}) \ge \lim_{N \to \infty} \sum_{k=1}^{N} \frac{J_{\rm ph}(E_k)\alpha(E_k)\Delta E_k}{I}$$
(6)

Because by virtue of eq 2 we have

$$\lim_{N \to \infty} \sum_{k=1}^{N} \frac{\alpha(E_k) \Delta E_k}{I} = 1$$

we can rearrange eq 6 as

$$\lim_{N \to \infty} \sum_{k=1}^{N} \left[J_{\text{ph}}(E_{\text{max}}) - J_{\text{ph}}(E_k) \right] \cdot \left[\frac{\alpha(E_k) \Delta E_k}{I} \right] \ge 0$$

Given that $J_{\rm ph}(E_{\rm max}) \ge J_{\rm ph}(E)$ by definition and because $\alpha \ge 0$, the terms in both square brackets above are positive, and so is the left-hand side. This proves the inequality in eq 5 and shows that the delta function $\alpha_{\rm opt}$ in eq 4 is the optimal absorption spectrum maximizing sunlight harvesting at very small absorber thickness.

For AM1.5 illumination, a physical system realizing such a delta-like absorption would show a single, strong absorption peak of small energy width (e.g., $\sim 10 \text{ meV}$) centered around $E_{\text{max}} = 0.8 \text{ eV}$ (see Figure 1b). It is clear that such a delta-like

absorption spectrum is optimal just at very small thickness as it only allows harvesting of a small fraction of $\sim 1\%$ of the total incident sunlight in a small energy window centered around 0.8 eV.

Case 2: Small to Intermediate Thickness. Because for small thicknesses the optimal spectrum is found by maximizing the overlap integral in eq 5, it is intuitive to propose a SMA proportional to the incident spectrum as the optimal solution at small thickness

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$$\alpha_{\rm sma}(E) = c \cdot J_{\rm ph}(E) \tag{7}$$

where *c* is a normalization constant. Not only is this solution intuitive as it maximizes the overlap with the incident radiation, it can also enable sunlight collection over a much broader photon energy range than the delta-like case and is thus better suited to harvest sunlight at small and intermediate thicknesses. Formally, the SMA solution in eq 7 solves a slightly different problem than defined above, one in which the overlap integral in eq 3 is maximized under the constraint that the square of α (as opposed to α itself) integrates to a constant, here called *I'*. This is seen by simple calculus of variations²³

$$\frac{\delta}{\delta\alpha} \left[\int_{E_g}^{\infty} J_{\rm ph}(E) \alpha(E) \, \mathrm{d}E - \lambda \left(\int_{0.3}^{4} \alpha^2(E) \, \mathrm{d}E - I' \right) \right] \bigg|_{\alpha_{\rm opt}} = 0$$

where λ is a Lagrange multiplier. The solution to this equation is $\alpha_{\text{opt}} = c \cdot J_{\text{ph}}(E) = \alpha_{\text{sma}}$. Despite the fact that our derivation guarantees that the SMA spectrum is optimal only for $\alpha L \ll 1$ and under a slightly different constraint than eq 2, we show below that it leads to effective sunlight harvesting at small as well as intermediate thickness, as also do absorption spectra with small deviations from α_{sma} .

Case 3: Large Thickness. For larger thicknesses than those discussed thus far, the optimal absorption spectrum α_{opt} is the one maximizing $J_{abs}[\alpha]$ for a constant integrated absorption *I*. We carry out this functional optimization²³ for arbitrary thickness by using a Lagrange multiplier λ

$$\frac{\delta}{\delta \alpha(E)} \{ J_{\rm bs}[\alpha](L) - \lambda [\int_{0.3\,\rm eV}^{4\,\rm eV} \alpha(E)\,\rm dE - I] \} \bigg|_{\alpha_{\rm opt}} = 0$$

The solution of this equation yields the thickness-dependent optimal absorption $\alpha_{opt}(E,L)$

$$\alpha_{\rm opt}(E, L) = \frac{I}{3.7} \cdot \left(1 - \frac{1}{L}\right) + \frac{1}{L} \log[J_{\rm ph}(E)]$$
(8)

Because we further need to impose $\alpha(E) \ge 0$ for absorption, eq 8 only solves the problem for $L \ge 1$. In this thickness range, the solutions vary continuously between the logarithmic spectrum obtained by setting L = 1

$$\alpha_{\rm opt}(E, L=1) = c' \cdot \log[J_{\rm ph}(E)] \tag{9}$$

where c' is a normalization constant,²⁴ and the solution for $L \rightarrow \infty$ (or, equivalently, $\alpha L \rightarrow \infty$) consisting of a normalized constant absorption spectrum

$$\alpha_{\rm opt}(E, \, \alpha L \to \infty) = \frac{I}{3.7} = \text{constant}$$

We observe that the logarithm of the incident spectrum is a fairly constant function of energy (see Figure 1b). It was obtained by setting L = 1, and we will see below that this solution is optimal for large optical thickness $\alpha L > 1$. On the



Figure 2. (a) Comparison of harvested sunlight versus reduced thickness for the four optimal absorption spectra found here. The absorbed sunlight J_{abs} is expressed as the percent fraction of the total incident sunlight. The reduced thickness quantifies the absorber thickness in units of absorption depth (see text). The shaded regions are expanded in the insets (b) and (c), where (b) covers the case of large thickness $\langle \alpha \rangle L > 1$ and (c) covers the case of very small thickness $\langle \alpha \rangle L \ll 1$. The legend and axes labels in (a) apply to the entire figure.

other hand, for $\alpha L \rightarrow \infty$, the optimal spectrum becomes a constant, thus representing an ideal panchromatic absorber, as shown in Figure 1b.

To summarize, the four optimal absorption spectra α_{opt} found in different thickness regimes are

1. $\alpha_{\text{opt}}(E) = I \cdot \delta(E - E_{\text{max}})$ for $\alpha L \to 0$

2. $\alpha_{opt}(E) = c \cdot J_{ph}(E)$ for $\alpha L \ll 1$ and up to intermediate values of $\alpha L \approx 1$ (see below) 3. $\alpha_{opt}(E) = c' \cdot \log[J_{ph}(E)]$ for $\alpha L > 1$

4. $\alpha_{opt}(E) = \text{constant for } \alpha L \to \infty.$

RESULTS AND DISCUSSION

Optimal Sunlight Harvesting. Figure 1b shows the four optimal absorption spectra derived analytically above and highlights key differences in their trends. We observe that as the thickness increases, the optimal absorption spectrum becomes broader. The delta-like spectrum found at very small thickness capitalizes on the maximum incident radiation at a specific energy. As the absorber thickness increases, it becomes more advantageous to collect sunlight over a wider energy range and in a more balanced fashion. As a consequence, for increasing thickness, the optimal spectrum becomes broader and gradually more constant as a function of energy. It evolves from a solarmatched spectrum for small to intermediate thickness to the logarithm of the incident flux (eq 9), which is a broad and rather constant function of energy. At even larger thickness, the ideal spectrum has a constant value throughout the energy range relevant for sunlight harvesting, thus representing an ideal panchromatic absorber. While the solar-matched and panchromatic spectra have been considered to be advantageous

previously,^{9,10,15-19} the logarithmic and delta-like optimal spectra are novel possibilities emerging from our quantitative treatment.

Next, we discuss numerical calculations of sunlight absorption as a function of thickness for the four optimal absorption spectra found here. Such numerical calculations confirm our analytic results and extend their scope. $J_{\rm abs}$ curves as a function of thickness were computed using numerical integration of eq 1 by employing the trapezoid rule with energy grids of less than 0.01 eV resolution. In our calculations, the optimal spectra were all normalized to the same value of I as in eq 2, and we adopted a procedure to compare sunlight harvesting for different spectra independent of the value of I chosen for the normalization. To this end, we computed $J_{\rm abs}[\alpha](L)$ in eq 1 and plotted it versus the reduced thickness L/L_D , namely, the thickness L expressed in units of absorption depths. An average absorption depth is employed, corresponding to the inverse of the average absorption spectrum

$$L_{\rm D} = \langle \alpha \rangle^{-1}$$

so that the reduced thickness $L/L_{\rm D}$ can be equivalently written as $\langle \alpha \rangle L$. We remark that by virtue of eq 2, the average absorption in the 0.3–4 eV range is simply $\langle \alpha \rangle = I/3.7$. Our approach of plotting $J_{\rm abs}[\alpha](L)$ versus the reduced thickness $\langle \alpha \rangle L$ is equivalent to computing²⁵

$$J_{\rm abs}[\alpha] \left(\frac{L}{\langle \alpha \rangle}\right) \tag{10}$$



Figure 3. (a) Normalized absorption spectra of four molecular absorbers of interest in thin-film PV. Also shown is the solar-matched absorption, obtained by rescaling the incident solar flux J_{ph} . (b) Absorbed sunlight J_{abs} for different absorption spectra as a function of reduced thickness. Absorbed sunlight is expressed as the fraction of the total incident photon flux absorbed by the material. The shaded region at small reduced thickness is expanded in (c), where the dashed line indicates a thickness of $0.1L_D$ used to extract the J_{abs} data in Table 1.

It can be seen by inspecting eq 1 that this quantity is independent of the normalization *I*; if the absorption spectrum is rescaled by a factor of *p*, the transformations $\alpha \rightarrow p\alpha$, $I \rightarrow pI$, and $\langle \alpha \rangle \rightarrow p \langle \alpha \rangle$ all take place, and eq 10 is invariant under such rescaling

$$J_{\rm abs}[\alpha] \left(\frac{L}{\langle \alpha \rangle}\right) \to J_{\rm abs}[p\alpha] \left(\frac{L}{p \langle \alpha \rangle}\right) = J_{\rm abs}[\alpha] \left(\frac{L}{\langle \alpha \rangle}\right)$$

where the last equality follows from the definition of $J_{\rm abs}$ in eq 1.²⁶

Figure 2 shows sunlight absorption for the four optimal spectra derived here and for a thicknesses of up to $5L_{\rm D}$ reaching absorption saturation. It is seen that the SMA is optimal at small to intermediate thicknesses of 0.01-2 absorption depths, covering an absorption in the range of 0.005-90% of incident sunlight. This is surprising in light of the fact that the SMA spectrum was derived by optimizing absorption at small thicknesses and for a constant integral of α^2 , as opposed to a constant integral of α as adopted in our numerical calculations. Figure 2b shows absorption in the very small thickness limit where $L \leq 0.01 L_{\rm D}$ and the absorbed sunlight fraction is less than 1%. We observe that for a thickness of up to $\sim 5 \times 10^{-3} L_{\rm D}$, the delta-like spectrum outperforms all other absorption profiles. This confirms that for a material with an extremely small thickness leading to less than 1% sunlight absorption, the optimal spectrum consists of a narrow absorption peak rather than a broad-band absorption profile. While this finding is interesting and counterintuitive, it is perhaps of limited practical relevance in both PV and photosynthesis where a significantly larger fraction of sunlight is commonly captured. Nonetheless, it is relevant here to characterize photosynthetic absorbers, as discussed below. Figure 2c shows absorption at large thickness values in excess of one absorption depth and thus near sunlight absorption saturation. We observe that the logarithmic and panchromatic absorption spectra can provide better sunlight harvesting compared to a solar-matched absorber at thickness values larger than $2L_D$ and $3L_D$, respectively. The SMA spectrum saturates slowly toward 100% absorption for $L > 2L_D$; the logarithmic and panchromatic spectra both reach 100% absorption for $L \approx 5L_{\rm D}$, while the SMA only achieves ~97% absorption for the same thickness. This behavior confirms the

result of our functional optimization in eq 8, thus showing that the logarithmic spectrum is optimal to collect sunlight in thick materials as it can outperform all other spectra (including the panchromatic) for $L > 2L_{\rm D}$. The counterintuitive fact that SMA is not optimal at all thicknesses restricts the applicability limits of the widely employed SMA paradigm to a thickness range of approximately $0.01-1L_{\rm D}$.

Article

In practice, average optical depths vary significantly across materials employed as sunlight absorbers. Our analysis shows that the crossover between the delta-like and SMA spectra for the optimal absorber occurs at a thickness of $L \approx 10^{-3} L_{\rm D}$, while the crossover between the SMA and the logarithmic spectra occurs at a thickness of $\sim 2L_{\rm D}$. For a material with a low average absorption of $\alpha \, \approx \, 10^2 {-} 10^3 \ {\rm cm}^{-1}$, a thickness of $10^{-3} L_{\rm D}$ corresponds to 10-100 nm, while for a material with higher $\alpha \approx 10^4 - 10^5$ cm⁻¹, it corresponds to a subnanometer thickness and thus to either a monolayer or a regime not physically realizable. Hence, our results indicate that materials with relatively weak optical absorption and a thickness of less than ~100 nm can achieve better sunlight harvesting if their absorption spectra consist of narrow peaks centered around 0.5-1 eV rather than being broad or solar-matched. On the other hand, for materials with stronger absorption of $10^4 - 10^5$ cm^{-1} , a SMA spectrum is optimal over a wide range of thickness values. Our analysis further suggests that for thick materials aimed at harvesting sunlight quantitatively, a material with a flat absorption profile, such as the logarithmic or panchromatic cases, is convenient for a thickness in excess of 1-2 absorption depths. In the remainder of the paper, we employ the results obtained so far to investigate specific problems of relevance in PV and photosynthesis.

Optimal Sunlight Absorbers in PV. Given the necessity to trade off sunlight harvesting and charge transport, PV devices often operate in the small to intermediate thickness regime where SMA is optimal. To assess the performance of different molecular absorbers employed in PV, a metric can be established for how close a given absorption spectrum is to the optimal SMA. In this spirit, we devised a solar-matchedness figure of merit F_{SM} , defined as the inverse of the integrated square deviation of the absorption spectrum α of a material under study from the ideal SMA spectrum α_{sma}

$$F_{\rm SM} = \frac{I^2}{\int_{0.3\,\rm eV}^{4\,\rm eV} [\alpha(E) - \alpha_{\rm sma}(E)]^2 \,\rm dE}$$
(11)

It follows from its definition that $F_{\rm SM}$ increases monotonically for absorption spectra with a smaller mean square deviation from the optimal $\alpha_{\rm sma}$. In addition, $F_{\rm SM}$ is invariant for a rescaling of the absorption spectra by a constant p, in the sense that if $(\alpha, \alpha_{\rm sma}) \rightarrow (p\alpha, p\alpha_{\rm sma})$, then $I \rightarrow pI$, and $F_{\rm SM}$ is unchanged. $F_{\rm SM}$ is thus independent of the normalization Ichosen for the spectra. As such, it can be used to unambiguously characterize materials starting from knowledge of their absorption spectrum $\alpha(E)$ in the energy range useful for sunlight absorption.

Next, we apply the $F_{\rm SM}$ figure of merit to study PV absorbers. Figure 3a shows the absorption spectra of four molecules recently employed in thin-film solar cells with above 5% efficiency, overlapped with the solar-matched spectrum. Experimental absorption data were obtained from the literature for the two conjugated polymers P3HT^{31,32} and PTB7²⁸ and the two small molecules N719¹² and DTS(PTTh₂)₂.²⁷ For these four molecules, we computed the $F_{\rm SM}$ figure of merit and separately the absorbed sunlight $J_{\rm abs}$ at a small reduced thickness of $\langle \alpha \rangle L \approx 0.1$, after normalizing all of the absorption spectra to the same integral *I*. Comparison of $F_{\rm SM}$ and $J_{\rm abs}$ for the different absorbers confirms that $F_{\rm SM}$ can correctly rank the four materials considered here according to their sunlight absorption, in the sense that increasing values of $F_{\rm SM}$ correspond to increasing values of $J_{\rm abs}$ (see Table 1). Figure

Table 1. Figures of Merit Computed Using Equation 11 for Four Molecules Used in Thin-Film Solar Cells with High Performance, Together with Their J_{abs} for a Small Optical Thickness Value of $\langle \alpha \rangle L = 0.1$, As Shown in Figure $3c^{a}$

	material	F_{SN}	1 J _{abs} (%	max)
solar	-matched	∞	17.	0
DTS	(PTTh ₂) ₂ (ref 27)	1.5	2 7.	8
PTB	7 (ref 28)	1.4	-8 7.0	0
P3H	T (ref 29)	1.3	.0 6.	3
N719	9 (ref 30)	1.2	.7 3.4	4
				-

^{*a*}Experimentally measured absorption data were from the references cited in the table.

3b-c confirms that the ranking based on $F_{\rm SM}$ is consistent with the ordering of the calculated $J_{\rm abs}$ for small thickness values up to approximately one absorption depth. This result indicates that the concept of solar matchedness of an absorption spectrum, interpreted as the minimization of the mean square deviation from $\alpha_{\rm sma}$ and the consequential maximization of $F_{\rm SM}$ can be employed to predict materials for optimal sunlight harvesting for thicknesses of up to $L_{\rm D}$.

On the other hand, we observe in Figure 3b that at larger thickness, J_{abs} does not follow the same ordering as F_{SM} . In particular, the rate at which the different absorbers approach their maximum J_{abs} value is dictated by their spectral width, while their J_{abs} saturation value is set by the gap. It thus follows that at large thickness of $L > L_D$, the sunlight harvesting curves for different absorbers intersect, changing the J_{abs} ranking compared to the one based on F_{SM} valid at small thickness. This restricts the capability to make predictions based on the solar-matchedness concept to materials with small to intermediate thicknesses of less than L_D .

As a result of our analysis, we propose a convenient protocol to rank materials for optimal sunlight harvesting with application to PV, artificial photosynthesis, and photocatalysis. The procedure consists of measuring or computing the absorption spectra of candidate absorbers, normalizing their spectra to the same (arbitrary) constant I as in eq 2, and computing the figure of merit F_{SM} using eq 11. As shown above, such a ranking based on $F_{\rm SM}$ reflects the ranking for absorbed sunlight among different thin-film materials. Our approach thus alleviates the need to experimentally measure absorbed photon fluxes or the resulting currents in multiple thin-film samples under simulated sunlight illumination. As such, it enables rapid screening of sunlight absorbers, both experimentally (without using simulated sunlight) and computationally. In particular, we suggest the possibility of screening materials for solar energy harvesting by employing accurate ab initio calculations of absorption spectra and using this information to establish a database of $F_{\rm SM}$ values for a large set of materials.

We remark that $F_{\rm SM}$ is a suitable figure of merit to rank sunlight absorption only at small to intermediate thicknesses of up to $L_{\rm D}$. On the other hand, eq 11 defines $F_{\rm SM}$ as the inverse of the integrated square deviation between the spectrum of the material under study and the optimal SMA spectrum. As a consequence, analogous figures of merit can be defined for different thickness regimes by replacing $\alpha_{\rm sma}$ in eq 11 with the optimal absorption for the thickness under study, to be chosen among those provided above.

The formalism developed in this work can provide the tools to optimize aspects of sunlight harvesting beyond those considered here. For example, if the geometry of the active layer differs from that of the flat absorber with absorbance $A(\alpha) = 1 - e^{-\alpha L}$ employed here, the form of the absorbance $A(\alpha)$ will also be different.³³ The optimization carried out here could be extended to arbitrary geometries by maximizing the functional $J_{abs}[\alpha] = \int \alpha(E)A[\alpha(E)] dE$ for the specific form of $A(\alpha)$ dictated by the geometry. The mathematical form of the problem suggests that optimal spectra for sunlight harvesting may vary significantly depending on the absorber geometry.

Sunlight Harvesting in Photosynthesis. All natural photosynthetic organisms contain sunlight harvesting antenna systems, in which specialized pigments collect solar energy and transfer it to a reaction center where photochemistry takes place.⁴ As the intensity of solar radiation changes by orders of magnitude during the day, the complex machinery at the basis of photosynthesis needs regulation mechanisms to function properly at different illumination levels. This property of photosynthetic systems can be regarded as a form of robustness against changes in sunlight illumination. At low light conditions, photosynthesis can be limited, and optimal sunlight harvesting becomes crucial. However, under bright to moderate sunlight intensity, the incoming photon flux can rapidly exceed the capacity of the photosynthetic apparatus to process the incoming energy. Excess energy must be rapidly dissipated to avoid detrimental effects for the photosynthetic organism. For example, in leaves in full sun, up to 80% of the absorbed energy must be dissipated to avoid serious damage to the plant.⁵ Plants have evolved a variety of mechanisms for dealing with excess energy, including nonphotochemical quenching pathways to prevent damage and repair mechanisms if damage to reaction center proteins has occurred.4

The presence of such regulation processes suggests that absorbers in plants may not benefit by maximizing sunlight absorption, especially given that sunlight is sufficient and redundant under a range of illumination conditions. Rather, it is interesting to explore whether the absorption spectra of photosynthetic pigments in plants can provide an advantage in terms of regulating absorbed sunlight under different illumination conditions or in the presence of damaged absorbing pigments.

For antenna systems in plants, the variation of incident sunlight intensity is caused both by changes in illumination during the day and by the fact that light intensity decreases exponentially with thickness within a leaf. This causes antenna systems positioned differently within the leaf to function under different incident sunlight intensities. Damage and repair are common processes in plants, also leading to fluctuations in the absorbed sunlight flux.

While leaves are overall opaque, single antenna systems in chloroplasts possess an overall absorbance of ~10–20%,¹³ corresponding to an optical thickness of $L/L_{\rm D} \approx 0.1-0.2$. Absorption in single antenna complexes thus falls in the small thickness regime characterized by a linear increase of sunlight harvesting with thickness, at a rate quantified by eq 3. The absorption spectra of photosynthetic antenna complexes in plants are a superposition of the absorption of different pigments. Among these, chlorophylls are commonly thought to have the role of main sunlight absorbers, while carotenoids play a key role in regulatory mechanisms.^{4,13}

The absorption spectra of the two most common pigments in plants, chlorophyll a (chl-a) and chlorophyll b (chl-b), were obtained from ref 34 and are shown in Figure 4a. The characteristic features of chlorophyll spectra are two absorption peaks at photon energies of ~1.8 and ~2.8 eV (red and blue parts of the visible spectrum, respectively) and small absorption values around 2.3 eV in the green. The spectra of chl-a and chlb show a poor overlap with the incident solar spectrum, corresponding to a value of $F_{\rm SM}$ = 0.96 computed here using eq 11. For comparison, the best molecular absorber studied here, $DTS(PTTh_2)_2$, has $F_{SM} = 1.52$ (Table 1). As shown in the analysis above, this result illustrates that sunlight harvesting is far from optimal for chlorophylls in photosynthetic complexes. This is confirmed by a direct comparison of sunlight absorption for chl-a and chl-b versus $DTS(PTTh_2)_2$ and the SMA absorber optimal in the small thickness regime (see Figure 4b).

Contrary to previous conjectures,¹³ our analysis highlights the dramatic differences between absorbing sunlight in narrow energy ranges (for example, with an absorption spectrum with poor solar matchedness as in the case of chlorophylls), as opposed to absorbing sunlight in a broader energy range with an absorption spectrum closer to the optimal SMA. Here, we showed this difference quantitatively by employing the $F_{\rm SM}$ figure of merit to rank absorbers based on the amount of sunlight harvested at small to intermediate thickness. Our results indicate that chlorophylls and other pigments with narrow absorption features are not optimal for sunlight harvesting in the small thickness regime typical of photosynthetic complexes. Recent work¹³ hypothesized that the narrow absorption features present in chlorophylls and other photosynthetic absorbers may optimize exciton transport, as one could reconcile using Förster theory.^{35,36} However, we note that on the basis of Förster theory alone, optimal exciton transfer rates would be achieved by an absorber with a single absorption peak at as small an energy as possible within the 0.3-4 eV range of solar radiation. This fact can be inferred by the form of the energy transfer rate k between two localized chromophores at a fixed distance within Förster theory



Figure 4. (a) Absorption spectra of chl-*a* and chl-*b*. The SMA spectrum is also shown for comparison. (b) Sunlight absorption of chl-*a* and chl-*b*, expressed as the percent fraction of absorbed sunlight out of the total incident flux. For comparison, absorption in a solar-matched absorber (namely, the optimal spectrum at small thickness) and of $DTS(PTTh_2)_2$ is also shown.

$$k \propto \int \frac{e(E)\alpha(E)}{E^4} dE$$
 (12)

where e(E) and $\alpha(E)$ are, respectively, the emission spectrum of the donor and the absorption spectrum of the acceptor as a function of photon energy E. In this formula, k is a functional of e(E) and $\alpha(E)$ and takes a form reminiscent of an overlap integral with an extra E^{-4} weighting factor. Similar to what was seen in the optimization of eq 3, k is maximal for a delta-like absorption and emission centered at an energy $E_{\rm max} \approx 0.5$ eV, the latter maximizing the E^{-4} factor within the solar energy range. This would be achieved by a molecule with a single absorption resonance at $E_{\rm max} \approx 0.5$ eV. On the other hand, the absorption spectra of chl-a and chl-b present two major absorption peaks at significantly higher energy than 0.5 eV. In addition, the emission spectrum of the chlorophyll donor after excited-state thermalization is centered around the lowestenergy peak at $E \approx 1.8$ eV, thus decreasing the overlap with the absorption spectrum of the chlorophyll acceptor presenting the double-peak structure. We conclude that the absorption spectrum of chlorophylls in plants does not maximize energy transport rates, while at the same time, it cannot maximize sunlight harvesting, as discussed above.

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On this basis, the reason why chlorophylls present two absorption peaks in the red and blue and little absorption in the green part of the visible spectrum remains to be elucidated. There may not be a specific reason or evolutionary advantage behind the shape of the absorption spectra of chlorophylls. However, we describe here two properties of the absorption spectra of chlorophylls that seem to be advantageous for a photosynthetic system, without speculating whether or not they are the result of evolutionary selection.

First, we observe that damage and repair processes lead to fluctuations in the concentration of sunlight absorbers in photosynthetic antenna systems and hence to fluctuations in their optical thickness $\langle \alpha \rangle L$. Thin-film absorbers such as chlorophylls with poor overlap with the solar spectrum show a much slower variation of sunlight absorption as a function of thickness, as quantified by the slope $\partial J_{abs}/\partial L|_{\alpha L \to 0}$ in eq 3. This trend is confirmed in Figure 4b, where it is seen that the slope of the J_{abs} versus thickness curves for chl-*a* and chl-*b* is smaller by approximately 1 order of magnitude compared to that of the more efficient $DTS(PTTh_2)_2$ and the optimal SMA absorbers. The smaller variation of J_{abs} in response to changes in the number of absorbers is an advantage for photosynthetic systems as it provides an intrinsic robustness against fluctuations related to damage and repair processes. For a representative area of $\sim 10 \ \mu m^2$ typical of a chloroplast, the number of absorbed photons is relatively small, in the range of 1000-10000 photons/s depending on incident sunlight intensity. Thus, even small variations in the number of absorbers can impact the mechanisms regulating photosynthetic activity. In this regard, the poor overlap of the absorption spectra of chlorophylls with the solar spectrum guarantees a minimal variation of the number of absorbed photons following changes in the number of absorbers. Such a strategy seems to be advantageous to minimize the impact of damage or pruning of chlorophyll molecules. Previous work has highlighted the robustness of energy transport against damage in photosynthetic antennas, although the form of robustness conjectured here is different and related to sunlight harvesting.

A second robustness mechanism is related to the variation of the incident sunlight $J_{\rm ph}$, commonly varying by orders of magnitude during the day. For a linear variation of the sunlight intensity such that $J_{\rm ph} \rightarrow p \cdot J_{\rm ph}$ (*p* is a real number), the absorbed photon flux $J_{\rm abs}$ varies linearly, as seen from eq 1

$$J_{abs}[p \cdot J_{ph}(E)] = p \cdot J_{abs}[J_{ph}(E)]$$
⁽¹³⁾

As a consequence, an absorber with a smaller J_{abs} will experience smaller variations in the absolute number of absorbed photons as a result of changes in the intensity of incident sunlight. On this basis, photosynthetic systems possessing a nonoptimal absorption spectrum achieve a superior robustness against external sunlight variations.

Taken together, these observations lead us to conjecture that the narrow peaks in the absorption spectra of chlorophylls may optimize aspects related to robustness rather than sunlight harvesting. We hypothesize that plants let go of a good portion of sunlight to attain a poor overlap with the solar spectrum. This in turn leads to a slower variation in the number of absorbed photons in response to internal (damage) or external (illumination intensity) changes. While these hypotheses need further investigation, our analysis appears to rule out the possibility that chlorophylls may be designed to achieve optimal sunlight harvesting in photosynthetic systems.

CONCLUSIONS

Our work formulates sunlight absorption in materials as a constrained optimization problem. We express the absorbed sunlight as a functional of the absorption spectrum to derive optimal absorption spectra. A key conclusion of our analysis is that the shape of the optimal spectrum depends on the geometry of the absorber. For a flat layer of a material, the optimal spectrum evolves from a delta-like solution for very small thickness to a flat panchromatic spectrum for large thickness near absorption saturation. For a wide range of thickness values of practical interest, a rigorously defined solarmatched absorption spectrum yields optimal sunlight harvesting. We employ this framework to study problems of interest in PV solar cells and photosynthesis. For PV, we propose a figure of merit based on the SMA concept that can be computed directly from the absorption spectrum and can successfully rank thin-film materials for best sunlight harvesting. Our work elucidates the concept of SMA and its applicability limits, proposes a formalism to design efficient sunlight absorbers, and sets the stage for accurate high-throughput screening of materials for solar energy harvesting. For photosynthesis, our analysis shows that chlorophyll absorbers commonly found in plants do not achieve optimal sunlight harvesting. On the other hand, their incomplete absorption of the solar spectrum leads to an inherent robustness related to a slower variation in the number of absorbed photons in response to damage or changes in the illumination intensity. Finally, we remark that an alternative approach to the analytical treatment carried out here would consist of maximizing sunlight absorption numerically by combining trial changes in the shape of the absorption spectrum with Monte Carlo or genetic algorithm optimization schemes. Combined with electromagnetism calculations, this could afford optimization of sunlight harvesting in heterogeneous materials of arbitrary geometry.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge financial support from the Solar Frontiers Program at MIT. We are grateful to XSEDE for providing computational resources.

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(25) Equivalently, one could normalize the absorption spectrum to obtain $\langle \alpha \rangle = 1$ and then study $J_{\rm abs}$ as a function of thickness *L*.

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